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THE NATURE OF ACTIVATION HEATS. A CALCULATION OF THE HEAT OF ACTIVATION FROM BAND SPECTRA DATA

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When one compares the heat of activation in a chemical reaction with the heats of dissociation of one of the reacting molecules into its component parts (*cf.* Tables I, II and 111), the conclusion may be drawn that activation is not, in general, a dissociation but must be essentially an interaction between two molecules, in which both take part and which could not occur except for the presence of the second molecule. In the present paper this idea will be applied in detail to the hydrogen iodide decomposition, as the

TABLE I

DISSOCIATION ENERGETICS

Activation heats taken from Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford, 1926. Heats of dissociation calculated from data in Tables II and III. Value for Cl + ClO taken as one-half "atomic" heat of formation of Cl_2O. Value in parentheses for H + I indicated from convergence limit [Tingey and Gerke, THIS JOURNAL, 48, 1838 (1926)], but uncorrected for the fact that absorbing molecules may be in a higher quantum state than the zero-th. Heat of activation for ammonia estimated (Hinshelwood, p. 93). Heat of activation for N_2O_5 decomposition given in parentheses corrected to ten degrees of freedom by formula

$$E_{\text{corr.}} = E_{\text{obs.}} + 2.303RT[((n/2) - 1)]$$

Substance	Products	Heat of dissociation, kg. cal.	Homogeneous heat of activation
N_2O_5	$N_2O_4 + O$	71	24.7
	$N_2O_3 + O_2$	20.2	
	$2NO + O$	251	
	$NO + NO_2 + O_2$	28.5	(30.4)
	$N_2O + 2O_2$	18.4	
	$N_2 + 2O_2 + O$	68	
N_2O	$N_2 + O$	48	59.4
	$N + NO$	110.5	
O_3	$O_2 + O$	35	26.0
Cl_2O	$Cl_2 + O$	52	21.4
	$Cl + ClO$	(55)	
HI	$H + I$	68.9 (64.4)	44.7
NH_3	$NH + H_2$	64.8	(70.0)

TABLE II

HEATS OF FORMATION OF THE ELEMENT MOLECULES

Substance	Kg cal.	Reference
H_2	101	Witmer, *Proc. Nat. Acad. Sci.*, 12, 238 (1926)
N_2	219	Mulliken, *Phys. **Rev.***, 32, 761 (1928) Birge, *Nature*, 122, 842 (1928)
O_2	139	Herzberg, *Z. physik. Chem.*, **4B**, 223 (1929) Birge, *Trans. Faraday Soc.*, 25, 707 (1929)
I_2	35 2	Kuhn, *Z. Physik*, 39, 77 (1926)
Cl_2	58 5	Kuhn, *Z. Physik*, 39, 77 (1926)
$C_{dia.}$	141	Kohn and Guckel, *Naturwissenschaften*, 12, 139 (1924)

TABLE III

ATOMIC HEATS OF FORMATION (*i.e.*, FROM THE GASEOUS ATOMS)

Group	N_2O_5	N_2O_4	N_2O_3	NO	NO_2	N_2O	Cl_2O	HI	NH_3	NH	O_3
Heat, kg. cal.	565	494	406	157	240	267	110	68.9 (64.4)	274.1	108 3	174

References: Landolt-Börnstein, "Tabellen," Vol. V, pp. 1485, 1490, 1493, 1495, 1496; Hodgman-Lange, "Handbook of Chemistry and Physics," 13th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1928, p. 574; Villars, THIS JOURNAL, 51, 2374 (1929).

experimental data[1,2] for this reaction are the most accurate, and it will be shown that we can account qualitatively for its heat of activation if we make use of certain simple principles taught by the quantum mechanics.

These principles are the following. First, Franck[3] has shown that the electronic excitation of a molecule takes place instantaneously compared to its vibrational period, and that the separation of the nuclei can be considered to remain unchanged during the light absorption.[4] Condon[5] extended this principle by assuming that, for most of the time, the nuclei occupied those positions at the extremities of their vibrations, as it was here that the velocity of their motions was least. He was successful in explaining certain peculiarities of the intensity distribution in band spectra which had been mystifying up to that time, and has since shown how these considerations are in harmony with the quantum mechanics.[6]

Second, one of the characteristic differences between the quantum mechanics and the classical mechanics has been that the former takes account of degeneracy introduced by the fact that an electron, for example, in the H_2^+ ion may belong as well to a second similar atom as to the first one and have the same energy value. This degeneracy causes a probability distribution of the electron between the two atoms; if we think of the separate atoms and not the molecule, as a whole, the electron can be considered as belonging to one atom at one moment; at a later moment it may

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[1] Bodenstein, *Z. physik. Chem.*, 29, 295 (1899).

[2] Kistiakowsky, THIS JOURNAL, 50, 2315 (1928).

[3] Franck, *Trans. Faraday Soc.*, 21, 536 (1926).

[4] Cf. also Villars, *Nature*, 123, 240 (1929).

[5] Condon, *Phys. **Rev.***, 28, 1182–1201 (1926).

[6] Condon, *ibid.*, 32, 858 (1928); *Proc. Nat Acad. Sci.*, *13*, 462 (1927).

change its allegiance to the other atom, although it does not change its position nor its energy. This idea may be extended to a system of atoms and it is just as reasonable to expect that two of these atoms may change their allegiance, provided the energy of the second state is equal to that of the first. Thus, in the decomposition of hydrogen iodide, if two molecules, H_aI_a and H_bI_b collide, two kinds of allegiance exchange are possible. After the collision, H_a may owe allegiance to I_b and H_b to I_a. This is similar to the case mentioned above of the molecular hydrogen ion. The energy perturbation arising in this case of degeneracy will account, in part, for the van der Waals attraction between the two molecules. But a second case is possible, where H_a may owe its allegiance to H_b and I_a to I_b. If this occurs, a chemical reaction has taken place.[7]

Our picture, then, of chemical activation, or rather of chemical reaction, for activation is concomitant with reaction, is that of a collision in which the nuclear separations of the atoms are such that the latter can change allegiance without changing their total energy content. Expressed in an equation, chemical reaction can occur only when

$$x + y - 1.4 = a + b \qquad (1)$$

where x and y are the internal energies of the two colliding hydrogen iodide molecules, a and b the internal energies of the hydrogen and iodine molecules, respectively, and -1.4 is the heat of reaction.[8] In the following calculations these energies are considered as representing vibrational energy only; they are the values obtaining at the moment just before and just after the exchange and do not account for any attractive or repulsive force between the hydrogen iodide molecules. Kinetic energy of the molecules after collision is considered equal to that before collision, since the probability of energy transfer by a collision of the second kind rapidly diminishes with increasing difference in the total kinetic energies.[9] Obviously, the energy of activation is

$$A = x + y + F \qquad (2)$$

where F is the potential energy due to repulsion of two hydrogen iodide molecules.

The calculation itself was a cut and try process. The vibrational potential energy curves were plotted for hydrogen, iodine and hydrogen iodide. The iodine nucleus defined the origin in the hydrogen iodide curve and was considered to be at rest. A one-dimensional collision was then depicted (Fig. 1) by bringing a templet of a second hydrogen iodide curve up within a definite distance of the first, corresponding to a possible nuclear

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[7] The same conclusion has been drawn independently by Langer, *Phys. Rev.*, 34, 92 (1929).

[8] Landolt–Börnstein, "Tabellen," Vol. V, p. 1489.

[9] Beutler and Josephy, *Naturwissenschaften*, **15**, 540 (1927); Webb and Wang, *Phys. Rev.*, 33, 329 (1929); Kallmann and London, *Naturwissenschaften*, 17, 226 (1929); *Z. physik. Chem.*, **2B**, 207 (1929).

separation of the iodine molecule. The energy value of b was read from the iodine curve (Fig. 2). Then, by means of a pair of dividers, the separations of the two hydrogen atoms, consistent with Equation 1 were found for different values of y ranging from 0 to 60 kg. cal.

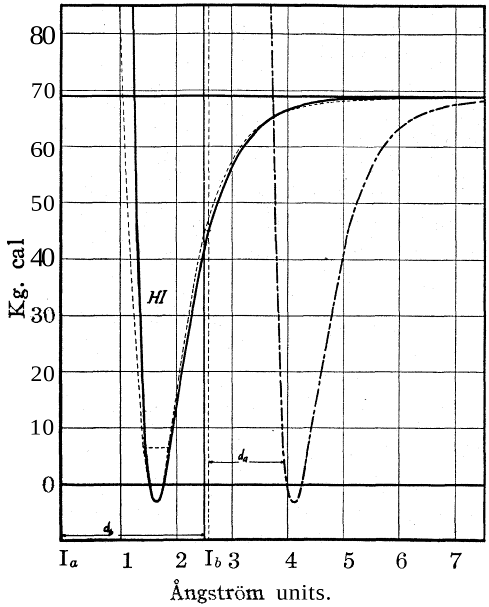

Fig. 1.—Vibrational potential energy curves of two colliding hydrogen iodide molecules. Heavy lines, Morse function. Dotted right branch, inverse power function. Dotted left branch, harmonic force function. Minimum distance of separation of iodine nuclei at collision d_b, is equivalent to b = 4 kg. cal., vibrational energy of I_2 molecule (See I_2 curve). In case first HI molecule has 45 kg. cal. vibrational energy ($y = 45$), second HI molecule must have x = 4 kg. cal., in order for relation $x - a = 1.4 + b - y$ and distance apart of H nuclei, d_a (equivalent to a = 43.5—see H curve) to be compatible. $A' \equiv x + y = 49$. First vibrational quantum level represented by dotted line. Band spectra constants used from Czerny, Z. Physik, **44**, 250 (1927). $\omega_0'' = 2272$ cm.$^{-1}$, $I_0'' = 4.309 \times 10^{-40}$ g. cm.^{2}; $r_0'' = 1.616 \times 10^{-8}$ cm.

Potential energy curves for hydrogen, iodine and hydrogen iodide were plotted by making use of band spectra constants which give us the various derivatives of the curve at the equilibrium position of the nuclei.[10]

By expressing the potential energy in the form of an inverse power series

$$V = (a_6/r^6) + (a_7/r^7) + (a_8/r^8) + (a_9/r^9) + (a_{10}/r^{10}) \qquad (3)$$

one can readily obtain the constants and calculate points for large nuclear separations.[11] This series is no longer convergent for small nuclear separations; the curve actually has several minima, some of which are lower than that corresponding to the stable state of the molecule. When data for iodine are substituted in the equations, the constant a_6 turns out to be positive, which is impossible.[12]

Morse[13] has proposed a new function

$$V = A + De^{-2a(r - r_e)} - 2De^{-a(r - r_e)} \qquad (4)$$

which has the advantage of having only one minimum point (at $r = r_e$), is of a form similar to those required by Heitler and London and

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[10] Born and Huckel, *Physik. Z.*, **24**, 1 (1925).

[11] Kemble and Zener, *Phys.* Rev., **33**, 532 (1929).

[12] Professor Kemble has kindly written me that this is quite likely due to inaccuracy in the value of α'' as reported by Loomis, ibid., 29, 119 (1927).

[13] Morse, *ibid.*, **34**, 57 (1920).

others, and the Schroedinger equation of which gives energy levels corresponding to those empirically observed. In this function, A is the heat of dissociation of the molecule, D the heat of dissociation plus the half quantum of vibrational energy associated with the lowest state of the molecule, r_e is the equilibrium separation of the nuclei in Ångström units, and

$$a = 2\pi\omega_e\sqrt{\frac{\mu}{2D}\frac{c}{h}} = 0.006547\ \omega_e\sqrt{M/D}$$

where ω_e is in cm.$^{-1}$, M the reduced mass in atomic weight units, and D is in kg. cal. This function has been used throughout these calculations and compares very favorably with the inverse power function (see Figs. 1 and 2).

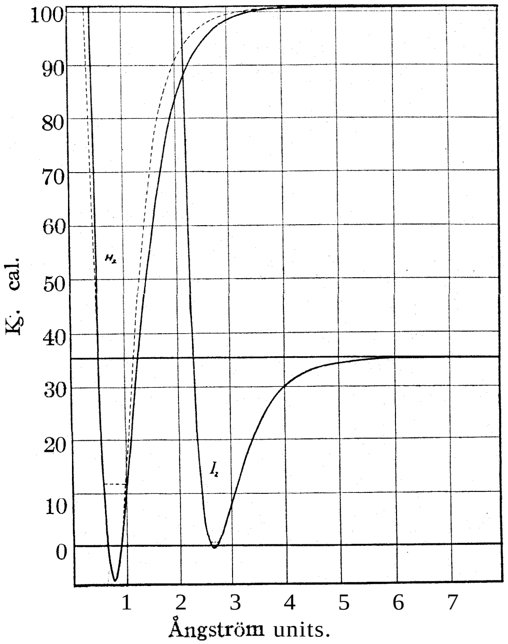

Fig. 2.—vibrational potential energy curves for hydrogen and iodine. Heavy lines, Morse function. Dotted right branch, inverse power function. Dotted left branch, ascending powers function. First vibrational quantum level represented by dotted line. Band spectra constants used: Hydrogen [Hori, *Z. Physik*, 44,834 (1927)]—$\alpha'' = 2.7$; $\omega_0'' = 4415.2$ cm.$^{-1}$; $I_0'' = 0.467 \times 10^{-40}$ g. cm.^{2}; $r_0'' = 0.75 \times 10^{-8}$ cm.; Iodine [Loomis, *Phys. Rev.*, 29, 119 (1927)]—$\alpha'' = 0.00012$; $\omega_0'' = 213.9$ cm.$^{-1}$, $I_0'' = 742 \times 10^{-40}$ g. cm.^{2}, $r_0'' = 2.66 \times 10^{-8}$ cm.

In the calculation procedure outlined above, there is a certain arbitrariness. One may note that rotation has been left out of consideration. This was done mostly to avoid complication, the postulate being made that the total rotational energy (as well as kinetic energy of translation) be the same after as before the collision. When we recall that hydrogen iodide molecules have a dipole moment,[14] it is seen that a rotation from the considered orientation at collision, I^--$H^+ \longleftarrow$ I^--H^+, through 180° to I--H f $\longleftarrow$ H^+-I^- would require the transformation of some of the available energy into orientation energy. This would have to be corrected for. Moreover, the faster the rotation, the less time is going to be spent by the molecule in those particular positions where reaction is favored, and hence the probability of reacting under such circumstances becomes negligibly small. A few cases were calculated corresponding to this 180° orientation away from the natural posi-

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[14] C. T. Zahn, *Phys. Rev.*, 24, 400 (1924): 27, 455 (1926).

TABLE IV

CALCULATED HEATS OF ACTIVATION FOR HI DECOMPOSITION

$x - a$ must $= 1.4 + b - y$

I-H ⟵ I-H

d_b	x	y	a	b	A'	d_b	x	y	a	b	A'	d_b	x	y	a	b	A'
2.3	69	20	53	35	89	2.35	59	20	57.5	20	79	2.4	67	14.5	67	13	81.5
	45	30	39		75		39.5	30	48		69.5		55	20	60.5		75
	32.5	36.4	32.5		69		15.5	40	34		55.5		35	30	50.5		65
	22	40	25.6		62		5	45	28.5		50		14	40	39.5		54
	12	45	19.5		57		0	50	31–21		50		0	50	25–36		50
	0	50	13.5		50								5	45	35.5		50
2.45	62	15	68	7.5	77	2.5	63	15	72	4	78	2.6	63	15	76.5	0	78
	52	20	63		72		52	20	66.5		72		55	20	73.5		75
	33	30	54		63		33	30	57.5		63		35	30	63.5		65
	13	40	44		53		14	40	48.5		54		17.5	40	56		57.5
	0	50	41–30		50		4	45	43.5		49		6.5	45	50		51.5
	5	45	41		50		0	50	45–33		50		0	50	52–43		50
2.7	68	15	81	0	83	2.8	65	20	82	1.6	85	2.9	37	40	71	4.5	77
	60	20	78.5		80		49	30	76		79		26	45	65		71
	40.5	30	69		70.5		30	40	67		70		15	50	59		65
	21.5	40	60		61.5		18	45	60		63		1.5	55	50.5		56.5
	11.5	45	55		56.5		8	50	55		58		63.5	25	82.5		88.5
	1.5	50	50		51.5		0	55	54–45		55		55.5	30	79.5		85.5
3.0	69	25	85	7.5	94	3.1	68	30	85.5	11	98	3.2	66	35	85.5	14	101
	61	30	82		91		52	40	79.5		92		59	40	83.5		99
	44.5	40	75.5		84.5		30	50	67.5		80		38	50	72.5		88
	34	45	70		79		0	60	48–57				7	60	51.5		67
	22	50	63		72												
	8	55	54		63												
	0	60	40–49														

TABLE IV (*Concluded*)

d_b	x	y	a	b	A'	d_b	x	y	a	b	A'	d_b	x	y	a	b	A'
3.3	65	40	85.5	18	105	3.4	69	40	88	19.5	109	3.5	66	45	87.5	22	111
	47	50	77.5		97		52	50	81		102		46	55	77.5		101
	15	60	55.5		75		20	60	59		80		28	60	64.5		88
													0	65	42–50		65

I-H ⟵ H-I

d_b	x	y	a	b	A'	d_b	x	y	a	b	A'	d_b	x	y	a	b	A'
2.3	36_i	20_o	19.5	35	56	2.35	18_i	10_o	6.5	20	28	4.2	65_i	0_o	32	31.5	65
	8.5_o	30_i	2		38.5		20_o	20_i	18.5		40		30_o	10_i	7		40
	41_i	$_o$	34.5		71		21.5_i	$_o$	20		41.5		30_i	$_o$	7		40
	29_o	40_i	33		69		39.5_o	30_i	48		69.5		13_o	20_i	0		33
	50_i	$_o$	53.5		90		26_i	$_o$	34.5		56		64_o	$_o$	51		84
	46_o	50_i	59.5		96		51.5_o	40_i	70		91.5		10_o	30_i	7		40
	57_i	$_o$	70.5		107		31.5_i	$_o$	50		71.5		40_o	$_o$	37		70
	32.5_i	10_o	6		42.5		62_o	50_i	90.5		112		15_i	$_o$	12		45
	13_o	30_i	6.5		43		39.5_i	$_o$	68		89.5		7.5_o	40_i	14.5		47.5
													59_i	$_i$	66		99
													63_o	$_o$	70		103
													50_i	$_o$	57		90

(i = inner branch)
(o = outer branch)

tion. It may be seen that sometimes the sum $A' \equiv x + y$ is smaller than the experimental heat of activation, but the difference is of the proper order of magnitude to be accounted for by the dipole repulsion.

Besides the repulsive force originating from a re-orientation of the molecule, there is a van der Waals attractive force between the molecules. The order of magnitude of the corresponding energy may be very roughly estimated from the latent heats of vaporization and fusion. The former is 4.7 (at −36°) kg. cal. and the latter 0.7[15] (at −51°). The density of the liquid at the boiling point is 2.799; this corresponds to an average separation of the molecules of 4.23 Å. A rough estimate of the separation of the molecules in the crystal lattice yields the same value.

The final results are summarized in Table IV. According to Bodenstein[1] the experimental heat of activation is 44 kg. cal. The minimum calculated values of A' lie in the neighborhood of 50 kg. cal. If we take $F = -5$ kg. cal., the agreement is very gratifying. In those cases where the vibrational quantum number of one of the molecules is very small, inaccuracies are especially prone to creep in, as the displacement of the nuclei has a much wider probability range than usual. The reader has, of course, recognized that quantization of vibration has also been neglected. In those cases of 180° relative orientation where some of the potential energy curves run parallel, it is especially difficult to pick the correct displacements, for here a small error makes a large energy difference. When we remember how rough the Condon working principle is, that the molecule spends all its time at the two extremities of vibration, the agreement in the calculated minimum values of A is very good and indicates that we have gained a better insight into chemical processes than has hitherto been possessed.

That enough molecules of these high vibrational energies exist to account for the observed reaction rate can be demonstrated by Hinshelwood's calculation.[16] He, it is true, made this on the assumption that it was translational energy alone (two degrees of freedom) which effected activation. One need only re-interpret his equations to mean vibrational energy alone and the same calculations hold.

Note of January 25, 1930.—Polyani has found some generalizations in regard to activation energies in reactions involving free atoms,[17] which may be understood in the light of the above theory. According to him, an exothermic reaction between a molecule and an atom demands no activation energy; on the other hand, an endothermic reaction between a

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[15] Giauque and Wiebe, THIS JOURNAL, 51, 1446 (1929).

[16] Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford, 1926, p. 92.

[17] Cf. also Nernst, "Die Grundlagen des neuen Wärmesatzes," Wilhelm Knapp, Halle, 1918, p. 133; Herzfeld, *Z. Elektrochem.*, 25, 301 (1919); *Ann. Physik*, 59, 635 (1919), in regard to bimolecular metatheses involving a free atom.

molecule and an atom will proceed with an activation energy equal to the heat of reaction. Thus, in the reaction

$$\begin{aligned} &H + \overset{69}{HI} = \overset{101}{H_2} + I + 32 \\ &y + 32 = a \end{aligned}$$

it is easy to find a collision distance at which the above equation will hold for $y = 0$.

On the other hand, in the reaction

$$\begin{aligned} &I + \overset{69}{HI} = H + \overset{35}{I_2} - 34 \\ &y - 34 = b \end{aligned}$$

it is obvious that in order for b to have positive values $y > 34$, and it is again easy to find a collision distance at which this equation will hold. The difference between this case and that taken up in the body of the paper lies in the extreme limitations to which we are subjected when we must satisfy the geometry of the *second* molecule taking part in the process.

Summary

Chemical reaction is most probable when the kinetic energy of the resulting molecules equals that of the reacting molecules, and will occur only in those cases where the sum of the potential energies of the colliding molecules plus the heat of reaction equals the sum of the potential energies which the resulting molecules would have if their respective nuclei undergo no change in position during the change in allegiance. The heat of activation, then, is the sum of the vibrational energies of the colliding molecules plus their heat of repulsion at the distance at which collision occurs. The foregoing principles have been applied to the hydrogen iodide decomposition with satisfactory numerical results.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL RESEARCH INSTITUTE, SHANGHAI, CHINA]

THE ANALYTICAL CHEMISTRY OF ELEMENT 91, EKATANTALUM, AND ITS DIFFERENCE FROM TANTALUM

BY ARISTID V. GROSSE

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In 1871 Mendelejeff,[1] on the basis of his periodic law, predicted the existence of a metal between thorium and uranium and named it ekatantalum (symbol Et). At present three isotopes of ekatantalum are known, all of them radioactive: brevium (Bv), discovered by Fajans[2] in 1913, protoactinium (Pa) and uranium Z (UZ, O. Hahn).[3]

Henceforth the author proposes to use as a synonym for element 91 the term "ekatantalum" (Et), meaning by it *all* of the isotopes of element 91. Under the term "protoactinium," according to its original meaning, will be understood only the parent substance of actinium, and by "brevium" only the disintegration product of UX_1.[4]

Brevium and uranium Z are very short-lived isotopes, their average life periods being 1.65 minutes and 9.7 hours. Naturally it is, and probably always will be, impossible to isolate them in pure form. Of the three isotopes, protoactinium is by far the most important, since it is the parent substance of actinium and all of the radio-elements of the actinium series. It was discovered in 1917 by Hahn and Meitner[5] in Germany, and simultaneously in England by the distinguished pioneer in radioactivity, Soddy in collaboration with Cranston.[6] Of the numerous radio-elements found since the splendid discovery of Mme. Curie, protoactinium is, in addition to radium, the only representative of a new radioactive chemical element which occurs in nature in considerable quantities. According to the author's latest determinations of the half-life period of protoactinium,[7] any uranium ore contains 0.6 g. of protoactinium for each gram of radium.

Until recently all attempts to concentrate and isolate the new element have been unsuccessful. These attempts have been based on the assumption that an analogy exists between the properties of ekatantalum and

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[1] D. I. Mendelejeff, *Ann. Suppl.*, 8, *172, 191, 203 (1871).*

[2] K. Fajans and O. Gohring, *Naturwissenschaften,* 1, *339 (1913); Physik. Z., 14, 877 (1913).*

[3] O. Hahn, *Ber.,* 54, *1131 (1921); Z. physik. Chem.,* 103, *461 (1922).*

[4] In this way the difference between the element "ekatantalum" and its isotope "protoactinium" will be emphasized, and such expressions as "protoactinium, free from brevium (or UZ)," or "brevium, free from protoactinium," will be definite.

[5] (a) O. Hahn and L. Meitner, *Naturwissenschaften,* **6**, *324 (1918);* (b) *Physik.* **Z., 19,** *208 (1918).*

[6] F. Soddy and J. A. Cranston, *Nature,* 100, *498 (1918); Proc. Roy. Soc. (London),* **94A, 384** *(1918).*

[7] Their description is in preparation. The most reliable value for the half-life period of protoactinium is *32,000* years ±10%.

tantalum similar to that between radium and barium. This assumption has been supported by the authority of many prominent chemists and was one of the principal reasons for failure in attempts to isolate ekatantalum. The fallacy of this assumption has been demonstrated in the course of this investigation, and therefore it will be discussed here in greater detail.

Fajans,[8] in 1913, worked on this assumption during the discovery of the first isotope of ekatantalum—brevium—and shortly afterward Hahn and Meitner[9] concluded that any analytical reaction of tantalum can be used for the separation of element 91 from other metals. In the same year A. Fleck,[10] at the suggestion of Soddy, made a thorough study of the chemistry of the radio-elements, and wrote: "The chemistry of UX_2 (element 91) remains extremely vague. Tantalum is generally recognized by chemists to be a very difficult substance to work with, and an element of higher atomic weight occupying a position in the same group is not likely to have more distinctive reactions."

The attempts of Hahn and Meitner[11] to discover the parent of actinium in pitchblende by adding tantalum and recovering it by the acid and hydrogen peroxide method, and similar efforts of Göhring[12] to separate the then hypothetical protoactinium together with tantalum from solutions of alkali tantalates obtained from pitchblende gave negative results.

In 1917 success was attained in the long search for protoactinium and it was found in tantalum preparations. The supposedly close analogy between element 91 and tantalum appeared to be confirmed, so that Paneth and Hevesy remarked in their well-known manual on radioactivity; "The chemical properties of protoactinium are exactly those which should be anticipated from a higher homolog of tantalum; accordingly, its separation from tantalum is difficult."[13]

Soon after their discovery, Hahn and Meitner succeeded in obtaining highly radioactive preparations, but these contained at most only 0.01 to 0.1% by weight of the new element.[14] These preparations consisted generally of varying amounts of oxides and phosphates of zirconium, hafnium, tantalum, columbium, titanium and some other metals. All efforts to raise the protoactinium concentration proved futile, and in 1926 Hahn,[15] emphasizing the importance of isolating element 91, stated: ". . . . but

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[8] Fajans and Göhring, *Physik. Z.*, 14, *880*, 882 (1913); Fajans, "Die Radioaktivität," **1919**, p. 42.

[9] Hahn and Meitner, *Physik. Z.*, **14**, 759 (1913).

[10] Fleck, *Phil. Mag.*, **26**, 534 (1913).

[11] Ref. 5b, p. 211.

[12] Gohring, *Physik. Z.*, **15**, 642 (1914).

[13] F. Paneth and G. Hevesy, "Lehrbuch der Radioaktivitat," **1923**, p. 159.

[14] Ref. 5 b, p. 214.

[15] Hahn, "Handbuch der Physik," **1926**, Vol. 22, p. 282.

protoactinium, as a homolog of tantalum, evidently has in an exceptionally high degree its annoying chemical properties. Instead of normal chemical reactions of precipitation and substitution, colloidal precipitations, peptizations and as yet insufficiently explained adsorptions take place. In addition, the quantities are always very small, as compared with the accompanying elements, tantalum, niobium, titanium, zirconium and others, so that until now it has not been possible to obtain protoactinium in a highly concentrated state."

Such was the situation when the author took up the problem at the end of 1926. Inasmuch as the law of Mendelejeff had been employed advantageously in previous work on the chemistry of metal-organic compounds,[16] it was also applied in this case, and in November, 1926 the writer presented to Professor O. Hahn a report entitled "The Properties of Protoactinium and its Compounds, Calculated According to the Periodic Law."[17] The principal deductions were as follows. (1) Element 91, ekatantalum, will have its own characteristic properties and analytical reactions, differing from those of tantalum and columbium, just as its neighbors, thorium and uranium, differ greatly in their properties from their lower homologs, hafnium and zirconium, and tungsten and molybdenum. (2) Ekatantalum pentoxide (Et_2O_5) will have basic properties (similar to UO_3 and ThO_2) and form salts with acids, as contrasted with tantalum pentoxide (Ta_2O_5), which is a weak acid anhydride.

These predictions were verified recently through the isolation by the writer of 2 mg. of element 91 in pure form as its oxide.[18] Ekatantalum pentoxide, like tantalum pentoxide, is a heavy white powder with a very high melting point. The ignited oxide is practically insoluble in concentrated sulfuric, nitric or hydrochloric acid.

The author has recently succeeded in extracting about 40 mg. of element 91.[19] Part of this material has been used in the experiments described herein, which aimed at a more detailed study of the analytical reactions of ekatantalum and especially a comparison with tantalum.

The Reactions of Element 91 and Tantalum

The analytical reactions of the two elements were carried out with comparable quantities (10–50 mg.) of the pure oxides. Thus the quan-

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[16] Grosse, *Z. anorg. allgem. Chem.*, **152,** 133 (1926); *Ber.*, **59,** 2646 (1926).

[17] This report is now in the possession of Professor Hahn, Berlin–Dahlem, Germany. A detailed account of the report was published in *J. Russ. Phys.-Chem. Soc.*, **60, 843** (1928).

[18] A. V. Grosse, *Nature*, **120,** 621 (1927); *Naturwissenschaften*, **15,** 766 (1927); *Ber.*, **61,** 233 (1928); *J. Russ. Phys.-Chem. Soc.*, **60,** *847* (1928).

[19] An account of the technical extraction of protoactinium from radium residues, carried out through the courtesy of the German I. G. Dyes Trust at one of its factories in Ludwigshafen on the Rhine, is now being prepared for publication.

tities of element 91 used were not very much smaller than the amounts used in ordinary quantitative analysis. In small beakers (10–25 cc.), the reactions of this rare metal may be observed and studied as easily as those of any of the commoner elements.

1. Material and Apparatus.—All chemicals were E. Merck's guaranteed pure reagents. All operations with hydrofluoric acid and molten sodium bisulfate were carried out in platinum dishes. Pyrex or Jena glassware was used.

The ekatantalum pentoxide (Et_2O_5) was part of the first **30** mg. of the pure material recently separated by the author. It had been freed from all other metals and especially purified for a new determination of the average life of the protoactinium atom. The β-activity of the oxide was taken as a criterion of its purity; it remained constant throughout the various purification processes.[20]

The tantalum pentoxide (Ta_2O_5) was a sample of pure oxide from Merck and contained only traces of columbium and titanium. For further purification it was dissolved in 40% hydrofluoric acid, potassium carbonate added, the potassium fluotantalate separated and washed with 1% hydrofluoric acid. This material was then fractionally crystallized three times from 1% hydrofluoric acid in platinum dishes, the first and last fractions being discarded each time. The product was treated with sulfuric acid to expel the hydrofluoric acid, fused with sodium bisulfate, the melt dissolved in cold water and the precipitated tantalum pentoxide washed with boiling water until free from alkali metals. The oxide was then dried and ignited to constant weight.

Procedure.—Dissolved or insoluble matter was determined by difference in weight (using a micro-balance) or, in the ease of element 91, also by estimating the amount of protoactinium electroscopically.[21]

Results

(a) Dissimilar Reactions

1. Reaction with Sodium Bisulfate and Sulfuric Acid.—Each oxide (10–50 mg.) was well mixed with 6–8 "times its weight of powdered anhydrous sodium bisulfate and carefully melted in a platinum crucible until all of the oxide had dissolved and the melt was absolutely clear. The cooled melt was then treated with 10–50 cc. of 3% sulfuric acid at room temperature. In the case of *ekatantalum* almost all of the oxide *goes into solution,* leaving only a small residue (I, 6%; II, 4%); while in the case of *tantalum* only a small part of the oxide dissolves, most of it *remaining* as a fine, white powder (residue: I, 84%; II, 79%).

2 and **3.** Reaction with Potassium Carbonate and Water.—Each oxide (10–50 mg.) was mixed with six times its weight of dry powdered potassium carbonate, melted and held in fusion with continuous stirring for ten to fifteen minutes. The oxide of *ekatantalum* is *insoluble* in the molten carbonate and remains suspended as a powder, giving the melt a milky appearance; *tantalum* pentoxide *dissolves completely* and clearly to give potassium tantalate.

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[20] The details of the purification methods will be published later.

[21] The method for exact determination of protoactinium and other isotopes of element 91 will be described in detail shortly.

The cooled melt was dissolved in 10–25 cc. of warm water (60–80°). The *ekatantalum* pentoxide remains as a fine, white *insoluble* powder (I, 99.9%; II, 99.8%), while the potassium *tantalate dissolves* to a clear solution with no residue.

4. *Reaction with Hydrogen Peroxide.*—*Ekatantalum* pentoxide hydrate is *completely precipitated* (99.9%) by an excess of hydrogen peroxide from a warm (40–60°) 2% sulfuric acid solution. On the other hand, a mixture of sulfuric acid and hydrogen peroxide *completely dissolves tantalum* pentoxide hydrate freshly precipitated from a potassium tantalate solution by sulfuric acid.

5. Reactions with Phosphoric Acid.—*Ekatantalum* pentoxide in solution in 20–30% hydrochloric acid, 15–20% sulfuric acid or in nitric acid, with or without hydrogen peroxide, is *completely precipitated* (99.9%) by an excess of phosphoric acid. A stable solution of *tantalum* pentoxide in concd. hydrochloric or sulfuric acid, with or without hydrogen peroxide, remains *absolutely clear* on the addition of an excess of phosphoric acid.

(b) Similar Reactions

6. Reaction with Ammonia.—*Ekatantulum* and *tantalum* in solution in mineral acids (hydrochloric, nitric, sulfuric and others) are *completely precipitated* on boiling with a slight excess of ammonia: Et_2O_5, 99.95%; Ta_2O_5, 99%. In the presence of *hydrofluoric acid or fluorides* the precipitation is incomplete (varying according to the concentration of ammonia, fluoride ion, etc.), owing to the formation of water-soluble double ammonium fluorides.

7. *Reaction with Hydrofluoric Acid.*—*Both oxides* are *completely dissolved* by 40% hydrofluoric acid on slow gentle warming, the ekatantalum pentoxide dissolving the more rapidly.

Discussion

A consideration of the reactions given above shows that except for the precipitation by ammonia, a reaction characteristic of almost all metals, *ekatantalum* and *tantalum* have *only one reaction in common*—*the* solubility of their oxides in hydrofluoric acid. (It is to be expected, of course, on the basis of the periodic law, that other reactions common to both will be discovered.)

Reaction 2 shows why Göhring[12] failed to isolate the hypothetical protoactinium together with tantalum, since actually he was purifying his tantalum preparations from the last traces of protoactinium which they may have adsorbed. Similarly, Reaction 4 indicates why the first attempts of Hahn and Meitner[11] were unsuccessful.

The behavior of the pentoxides of the two metals toward various reagents shows that while tantalum pentoxide is a feeble acid anhydride and forms more stable compounds with alkalies, ekatantalum pentoxide is a weak but decidedly basic oxide with no acidic properties.

All in all it may be said that the predictions made by the writer in 1926 as to the analytical properties of element 91 have thus far been proved by experiment; the expected characteristic properties of ekatantalum have been demonstrated. Once more Mendelejeff's law has proved its usefulness, and its application has rendered comparatively simple the solution of an apparently difficult task.

Summary

1. The unsuccessful attempts to isolate and obtain element 91—ekatantalum—were based on the assumption that it resembles its lower homolog—tantalum—just as radium resembles barium. The origin and development of this assumption and its contradiction to conclusions derived from the periodic law are discussed.
2. A study of the analytical chemistry of ekatantalum has been made with adequate amounts of its pure oxide. Its difference from tantalum predicted by the author on the basis of Mendelejeff's law, has been proved experimentally.
3. The behavior of ekatantalum toward different reagents is, in most of the cases observed, opposite to that of tantalum.
4. Ekatantalum pentoxide (Et_2O_5) is a distinctly, though feebly, basic oxide without acidic properties, whereas tantalum pentoxide (Ta_2O_5) is an acid anhydride and readily forms stable salts with basic oxides.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF UTAH]

THE BOILING POINTS OF CONSTANT BOILING HYDROCHLORIC ACIDS

BY WALTER D. BONNER AND ROLAND E. WALLACE

RECEIVED DECEMBER 5, 1929 PUBLISHED MAY 8, 1930

In connection with the work on the composition of constant boiling hydrochloric acid, recently published from this Laboratory,[1] we have made a precise determination of the boiling points of these acids over the same pressure range. The samples used were those whose analyses are given in the previous paper.

Foulk and Hollingsworth have shown[2] that the variation in boiling point of the acid which distils unchanged in composition at 750 ± 0.2-mm. pressure is not more than 0.003°, though they were not able to fix the temperature of boiling. In the work reported here a precision of 0.1 mm. was

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[1] Bonner and Titus, THIS JOURNAL, 52, 633 (1930).

[2] Foulk and Hollingsworth, *ibid.*, 45, 1224 (1923).

attained in the pressure control. This corresponds to a precision of temperature measurement of 0.021° at the lowest pressures, 50 to 150 mm. Above this pressure the boiling point curve rapidly flattens out, so that at 370-mm. pressure the temperature measurement has a precision of 0.007°, and at 760-mm. pressure one of 0.004°.

This is not, of course, so great a precision as that with which the vapor pressure of water is known. On the other hand, it is interesting to observe that with the apparatus we used it is much easier to obtain reproducible measurements with these acids than with either water or benzene. We suggest that this may be due to the binary solution overheating less readily than does a pure substance. Whatever the reason, it is an experimental fact that these acids yield more convenient fixed thermometric points than does water.

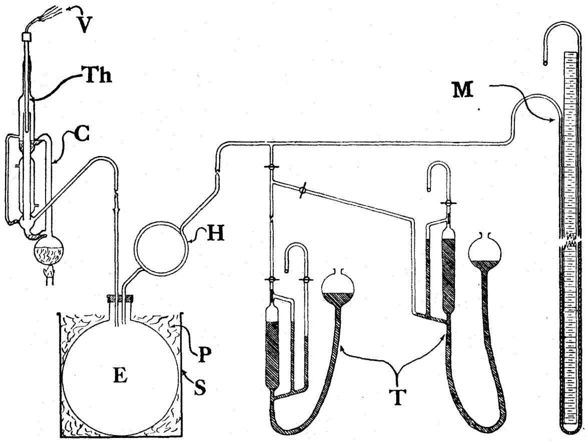
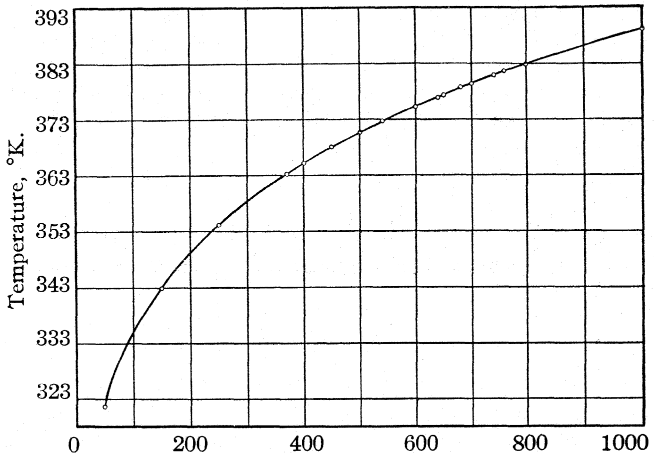


Fig. 1.—Apparatus. V, to bridge; Th, thermometer; C, boiling flask; H, glass spiral; P, paper packing; S, stone crock; E, 5-liter equilibrium flask; T, Toepler pumps; M, manometer.

Experimental

The apparatus, shown diagrammatically in Fig. 1, consisted of a pressure control device, a boiling flask and a platinum resistance thermometer. The pressure control device was essentially two Toepler pumps, the one to force air into the apparatus, the other to pump it out. The entire apparatus was of pyrex. All joints were either sealed or ground, with the exception of the entrance of the resistance thermometer, which was made tight with wrappings of rubber dam. The boiling flask was very kindly supplied by Professor C. A. Kraus, of Brown University. It was designed to minimize loss of distillate and to prevent superheating. The resistance thermometer was calibrated by the United States Bureau of Standards.

It was checked by us at the steam point and found to be exact. It was calibrated and used as a four-lead potential terminal resistor, with current reversing commutator. For this latter purpose we used a very heavy three-pole double-throw switch. Care was taken to have the leads from the commutator to the bridge heavy and of the same length. A radiation shield was not used, but the boiling point apparatus was carefully wrapped with heavy asbestos cord over the part containing the thermometer. Resistances were determined to 10^{-5} ohms by means of a calibrated Leeds and Northrup temperature bridge, of the Mueller type. The check on the steam point of the resistance thermometer was taken to be also a check on the calibration of the bridge. A high sensitivity D'Arsonval galvanometer, with lamp and scale at a distance of four feet, was used as the null instrument. The manometer in the pressure control device was very carefully made and calibrated. The mercury was twice distilled before being put into the apparatus. The two meter scale, of flat grained maple, was compared over its entire length with a standard meter. In making our calculations we have taken into account all essential corrections. The barometer used was of the Fortin type, carefully calibrated, and compared with the United States Weather Bureau instrument in Salt Lake City.



Pressure in millimeters of mercury.

Fig. 2.

Each sample of hydrochloric acid was introduced into the clean, dry boiling flask. After sealing the apparatus, the pressure was roughly adjusted to within 5 mm. of the pressure at which the sample had been prepared. When the sample had boiled for ten to fifteen minutes, the pressure was very carefully adjusted to within 0.1 mm., all essential calibrations and corrections being considered. The sample was then allowed to boil for an hour before any readings were attempted. In that time the thermometer had assumed the temperature of the condensing acid vapors, and its resistance was therefore constant. From the resistance of the thermometer the temperature was calculated, in accordance with the constants of the instrument and Callendar's equation. The boiling points so obtained are given in Table I and in the graph, Fig. 2.

TABLE I

BOILING POINT DATA

Press , mm	Boiling point, °C	Density, 25°	HCI, %	Press., mm	Boiling point, °C	Density, 25°	HCI, %
50	48 724	1 1118	23 42	640	103 967	1.0973	20.507
150	69 956	1 1073	22 520"	680	105 564	1 0968[a]	20.413
250	81 205	1 1042	21 883	700	106 424	1 0966	20.360[a]
370	90 237	1 1016"	21 365"	740	107 859	1.0962"	20.268
400	92 080	1 1010	21 235"	760	108 584	1 0959	20.222
450	95029	11002	21075"	800	110007	1 0955	20.155
500	97 578	1 0993	20 916	1000	116 185	1 0933	19.734
540	99 653	1 0987	20 777"	1220	122 98[a]	1 0915	19.358
600	102 209	1 0980	20 638"				

[a] Interpolated

Acknowledgment.—This work was assisted by a grant from the Warren Fund of the American Academy of Arts and Sciences, which we gratefully acknowledge.

Résumé

We have determined the boiling points of constant boiling hydrochloric acid at pressures between 50 mm. and 1220 mm. Pressure was maintained constant to 0.1 mm. and resistances were determined to 10^{-5} ohms. The temperatures given are precise to 0.02° for the lowest pressures and to 0.004° for pressures in the neighborhood of 760 mm.

SALT LAKE CITY, UTAH

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

A METHOD FOR THE DETERMINATION OF SURFACE AND INTERFACIAL TENSION FROM THE MAXIMUM PULL ON A RING

BY WILLIAM D. HARKINS AND HUBERT F. JORDAN

RECEIVED DECEMBER 6, 1929 PUBLISHED MAY 8, 1930

1. Introduction

Although many thousands of measurements have been made to determine the pull necessary to detach a ring from the surface of a liquid, it is a surprising fact that *until three years ago there was no "ring method" for the measurement of surface tension.* Thus in "International Critical Tables," nine experimental methods for surface tension are listed but a ring method is not included, since the procedure which had been designated by this term did not supply even one single measured value of surface tension of these tables.

The failure of the ring procedure was due to the fact that the theory had not been sufficiently developed to permit its use as a method of measurement, although an incomplete theory had been developed by Cantor,[1] Lohnstein,[2] Lenard,[3] Tichanowsky[4] and MacDougall.[5]

In 1926 Harkins, Young and Cheng,[6] on the basis of the well-justified assumption that the capillary height method, properly applied, gives correct values for the surface tensions of suitable liquids, showed how the ring procedure could be used as a moderately accurate method for such measurements. In the present paper the method is given a still higher degree of accuracy (about 0.25%).

In a third paper from this Laboratory, Drs. B. B. Freud and Henrietta Zollman Freud convert this into an absolute method, since by the use of the fundamental differential equation of Laplace they have been able to calculate the shapes of the surfaces upheld by rings. It is of considerable interest that their theoretical and our experimental procedure agree within approximately the limits of accuracy of either, that is, to about 0.25%, where the two have been compared.

Symbols

γ = surface tension in dynes per centimeter
a = square root of the capillary constant

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[1] Cantor, *Wied. Ann.*, 47, 399 (1892).

[2] Lohnstein, *Ann. Physik*, 25, 815 (1908).

[3] Lenard, *ibid.*, **74**, 395 (1924).

[4] Tichanowsky, *Physik. Z.*, 25, 300 (1924); 26, 523 (1925).

[5] MacDougall, *Science*, [N. S.] 62, 290 (1925).

[6] Harkins, Young and Cheng, *ibid.*, 64, 333 (1926).

M = weight of liquid raised above the free surface of the liquid; M = maximum value of M
P = total pull on the ring in dynes = Mg; $\mathrm{P} = Mg$
p = P divided by $4\pi R$; $\mathrm{p} = \mathbf{P}/4\pi R$
R = radius of the ring measured from the center of the ring to the center of the wire
r = radius of the wire
V = the volume of liquid raised above the free surface of the liquid, or $M/(D - d)$ V = maximum volume
D = density of the liquid
d = density of air saturated with vapor of the liquid
S = shape of the surface
h = the "pressure height" or the vertical distance from the point in the meniscus under the center of the ring to a point in the liquid where the pressure is equal to that in the vapor at the same level

In much of the earlier work the entirely false assumption was used that the maximum pull (p) per cm. on the ring is equal to the surface tension of the liquid-or

$$\mathrm{P} = Mg = 4\pi R\mathbf{p} = 4\pi R\gamma \qquad (1)$$

in which $\mathbf{P}$ is the total maximum pull on the ring as determined by the balance.

The results obtained by the use of this entirely incorrect equation vary from 30% too high to 30% too low, and even more. The high values are commonly obtained for surface, and the low for interfacial, tensions.

Harkins, Young and Cheng considered that the size of the surfaces outside and inside the ring is determined mostly by the size of the ring (R), and that its shape is determined by the surface tension and density of the liquid, the radius of the ring (R) and of the wire (r), and certain other variables. In order to determine the form of the functional relation they used the principle of similitude, which in this case indicates that the shape of each surface supported by the pull of the ring depends entirely, when at rest, upon a few simple dimensionless variables. These are (1) the ratio (R^3/V) of the cube of the radius of the ring to the volume of the liquid; (2) the ratio (R/r) of the radius of the circular ring to the radius of the circular wire of which it is made, and (3) the ratio (h^3/V) of the cube of the "pressure height" to the volume of liquid which the ring supports. Thus, the shape S is given by

$$S = f\,(\mathbf{R}^3/V,\ R/r,\ h^3V), \text{ or}$$
$$S = \varphi(R/a,\ R/r,\ h/a)$$

The surface tension is a function of the shape, and, therefore, of these same variables, and its value is given by the equation

$$\gamma = \frac{Mg}{4\pi R} \times f_1(R^3/V,\ R/r,\ h^3/V)$$

Since the volume upheld by the ring becomes a maximum at a certain definite shape for which the value of h^3/V is determined by the values of R^3/V and R/r

$$\gamma = \frac{\mathbf{M}g}{4\pi R} \times \alpha(R^3/V,\ R/r), \text{ or}$$
$$\gamma = \frac{\mathbf{M}g}{4\pi R} \times \frac{\gamma}{\mathbf{p}} = \frac{\mathbf{M}g}{4\pi R} \times F$$

The values of F may be determined experimentally by determining the true surface tensions of various liquids by the capillary height or drop weight methods, and comparing with the values of **p** as shown in the above equation.

A number of values of F were determined experimentally by Harkins, Young and Cheng, and it was shown that if R/r is held constant by regulating the dimensions of the rings, F varies with R^3/V along a smooth curve, regardless of the values of R. However, this work was not sufficiently extensive or precise for general use with accurate data.

2. Outline of Procedure

The present work is a thorough investigation of the technique of the ring method, and the accurate determination of the correction curves which were found in a preliminary way by Harkins, Young and Cheng.

The general method of procedure was to determine the surface tension of water, of benzene and of bromobenzene by the capillary height method, and the values of **p** for these liquids by the use of sixteen different rings, with values of R between 0.4 and 1.8 cm., of r between 0.009 and 0.05 cm. and of R/r between 13.9 and 78.3. The quantities $\gamma/\mathbf{p}$ and $R^3/\mathbf{V}$ were calculated and plotted against each other, and the curves so obtained for the various rings were corrected to even values of R/r. Thus curves for R/r equal to 30, 40, 50, 60 and 80 were obtained. Interpolated curves were also obtained for intermediate values of R/r.

The liquids water, benzene and bromobenzene were chosen for the standardization for the following reasons: first, because their contact angles against glass and against platinum also are zero, and their surface tensions may, therefore, be accurately determined by the capillary height method; and second, because they are easily purified and kept in the pure condition. While pure liquids were not required for the purposes of standardization as long as the same sample of liquid was used throughout and its true surface tension known, it was considered desirable to use pure liquids so that the surface tension values may be compared with those obtained by others.

3. Determination of the Surface Tension of Liquids by the Capillary Height Method

The surface tension of each liquid used in this investigation was determined by capillary height measurements made on very pure liquids. The method applied was similar to that of Richards and Coombs, Harkins and Brown and Young and Gross. The apparatus was exactly that of the last-named investigators, except that a special stopcock (S, Fig. 1) was inserted between the trap (T) and the large tube (I,), to facilitate the drying of the capillary. The average radius of the capillary, a 3-cm. section of a tube selected by Harkins, and Brown, and Davies, was 0.02557 cm. and of the large tube 1.805 cm. The mean diameter of this tube had been determined by these investigators, but was recalibrated by us at 26 levels by a determination of the capillary height with pure water at 25°, at which temperature its surface tension is 71.97 dynes per cm.

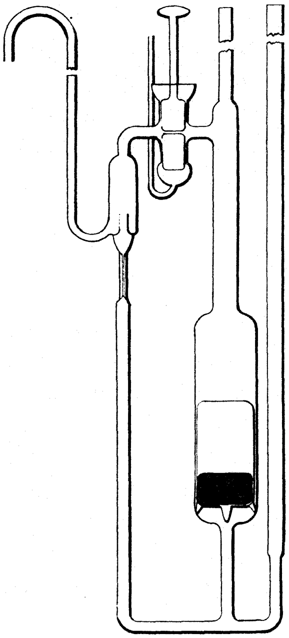

Fig. 1.—Capillary height apparatus.

The observed heights were corrected by adding $^1/_3\ r$ to correct for the volume of the small meniscus, and by adding 0.0018 cm. to correct for the rise in the larger tube when water was used. This latter correction was negligible with the other liquids.

Six values for the surface tension of benzene at 25° were obtained as follows: 28.19, 28.24, 28.23, 28.24, 28.24, 28.23, with a mean value of 28.22 dynes per cm. The density 25/4° was 0.8733, and $D - d = 0.8718_7$ was used.

For bromobenzene the values are: 35.75, 35.73, 35.75, 35.73, 35.75, 35.73, 35.75, 35.76, 35.77, 35.77, or a mean of 35.75, at 25°. The density was 1.4887 (25/4°), and $D - d$ was taken as 1.4875.

4. Apparatus for the Ring Method

The rings were made of platinum–iridium wire containing 10% iridium to give the wire stiffness, with the exception of rings 15 and 16. These contained no iridium, and proved to be unsatisfactory for practical purposes. It was found necessary to use wire of this alloy, as platinum wire bends too easily and rings made of it soon lose their shape through handling. The rings were constructed by bending the wire around a brass rod turned down to the exact inner diameter desired, and welding the ends of the wire together with a spot welder. This has to be done with extreme care or the wire will be flattened at the spot of the weld. The stirrups were then welded on to the top or side of the ring, and all protuberances and unevenness removed with a fine file and emery paper. In four of the rings, made with fine wire, silver solder was used instead of welding. The loop at the top of the stirrup was made in the form of an ellipse with the least possible radius of curvature at the uppermost part, so that the ring would always hang in the same position. All the rings with radii greater than 0.8 cm. were made with two stirrups whose planes were at right angles to each other.

It was found that the DuNoüy tensiometer is too inaccurate for measurements of the high precision desired in the present investigation. Therefore, a chainomatic balance, sensitive to 0.05 mg., was adapted for the work. The left pan was removed and a hole three-eighths of an inch in diameter was bored in the base of the balance directly under it, through which an aluminum rod connected the ring with the beam of the balance. The righ-hand pan was replaced by a very light aluminum pan, in order that the momentum of the beam and pan might be reduced to a minimum. The pan rest was disconnected, as it was found to be troublesome in making measurements.

In order to prevent ripples in the surface of the liquid, which might have been formed by lowering the level of the liquid or the containing vessel, a machine was devised to lower and raise the balance with great ease and smoothness. While such a machine is not essential to measurements by the ring method, it was deemed advisable to use it in this work in order to remove the source of error mentioned above. The machine is represented diagrammatically in Fig. 2. It consists essentially of four heavy upright steel rods, which are screwed into a heavy cast-iron base provided with leveling screws. Fitted onto these rods are two heavy bronze castings. The lower one is fastened to the rods, and supports the set of gears which raise and lower the upper movable casting. To the upper casting are attached the balance platform and its counterweight. Frictional effects were reduced to a minimum by a delicate counterbalancing of weights throughout. For example, the balance is counterbalanced by the movable weight W′. These and the casting which supports them are. in turn, counterbalanced by the weight W. This is connected to the upper casting by a steel piano wire which runs over a stationary pulley. The smoothness of operation was also increased by reducing the bearing surface of the movable casting to a minimum The balance platform is provided with two large oval-shaped openings, through which the rod connecting the ring with the balance beam passes.

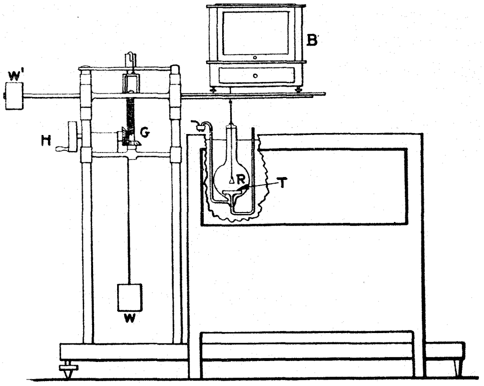

Fig. 2.—Apparatus for determination of surface tension by the ring method.

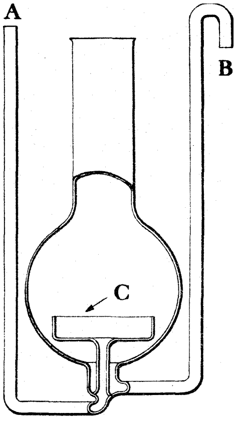

Fig. 3.—Flask for the ring method.

The flask used in the measurements is illustrated in Fig. **3.** The principle involved in the design is to provide a means of overflowing the surface to prevent surface contamination. The flask was constructed by sealing a cup (C) 7.5 cm. in diameter and 2 cm high near the bottom of a two-liter flask, and by replacing the neck with a longer and wider one The liquid is introduced in the side-arm **(A)** and the excess withdrawn through (B).

5. Measurement of Rings

Since the correction factor $(\gamma/p$ or $F)$ is a function of the variable R/r, it is necessary to have very accurate measurements of the radii of the wires of which the rings are made, as well as of the radii of the rings.

The diameters of the rings were measured by a screw micrometer carrying a microscope with *a* magnification of ten diameters. One division on the screw head corresponds to 0.0005 cm. The instrument had been originally calibrated by Dr. E. H. C. Davies, by comparison with a standardized invar scale by a series of 5000 measurements, and later checked by Mr. Frank Frese. In order to make precise measurements it is necessary to illuminate the ring from below, and the method was as follows, A reading glass about two and one-half inches in diameter was mounted in a hole in the top of a box, and within the box at the principal focus of the lens was placed a 100-watt lamp painted black with the exception of a spot about a centimeter in diameter. This provided for practical purposes a point source, with parallel light coming through the lens. Above the lens and about two inches away from it was placed the leveling table containing the ring. This was constructed as is shown in Fig. 4. It may be leveled with leveling screws, or, with the leveling screws removed, may be attached to a microscope by removing the microscope platform. In the top of the cylinder in the table was mounted a transparent celluloid disk (D), roughened with emery paper. The disk had two slits cut in it at right angles to each other (S) through which the stirrups were passed, and on it were scratched a series of concentric circles (C) to aid in centering the ring. Measurements on the rings were made across twelve evenly spaced diameters from the outer edge of the ring on one side to the inner edge on the other. Readings were taken at the point where the cross-hair, which had been previously made perpendicular to the direction of travel, became tangent to the edge of the ring.

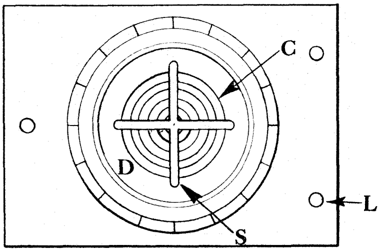

Fig. 4.—Apparatus for measurement of diameter of rings.

The measurements of the radii of the wires were made with a microscope, with a magnification of ten diameters and provided with a micrometer eyepiece. This was calibrated by comparison with an invar scale standardized by the Bureau of Standards. One division on the micrometer screw head corresponds to 0.0001 cm. at this magnification. In these measurements the leveling table was attached to the microscope in place of the microscope platform by means of a special adapter, and the illumination from below was used as in the previous measurements. In place of the celluloid disk a piece of bond paper was stretched over the top of the cylinder. In order to make the ring appear very black and the edges sharp, a narrow strip of thin cardboard with a slit very slightly wider than the diameter of the wire was slipped under the wire to cut down the extra light. This method gives excellent illumination, and precise measurements of the wire can be made in this manner. Measurements at twelve different, evenly spaced points on the ring were made and the average of these was used. The values for the radii of the rings and the radii of the wires are given in Table I.

TABLE I

RADII OF RINGS

No. of ring	R	r	R/r	No. of ring	R	r	R/r
1	0.4143	0.01070	38.72	9	0.4678	0.01607	29.11
2	.6065	.00903	67.17	10[a]	0.6366	.01570	40.55
3	.5103	.00973	52.45	11	1.5245	.02946	51.75
4	.8078	.01877	43.04	12	1.8277	.02986	61.21
5	1.0142	.02001	50.69	13	1.1806	.04009	29.45
6	1.2185	.02008	60.68	14	0.7759	.02578	30.80
7	1.2144	.02913	41.69	15	0.9421	.01585	59.44
8	0.6767	.04875	13.88	16	1.2603	.01610	78.28

[a] Ring number 10 was the ring furnished with a DuNoüy Tensiometer.

6. Measurement of Surface Tension by the Ring Method

The difficulties involved in making precise measurements by the ring method are far more numerous than most investigators have assumed. Any rigorous theory of the ring method would require: (1) that the wire of the ring lie in one plane; (2) that the plane of the ring be horizontal; (3) that the vessel containing the liquid under investigation be large enough so that any curvature of the free surface of the liquid would not be great enough to affect the shape of the liquid raised by the ring; (4) that the surface of the liquid be free from wave motion; (5) that there be no motion of the ring except an infinitesimally slow upward motion; (6) that there be no evaporation and consequent cooling of the surface; and (7) that the ring be round. These are requirements that are inherent in the proper technique of the ring method, and must be approximated as nearly as possible. Of these sources of error, the last is probably the least important.

The most important source of error arises from the ring not being horizontal. This was investigated in a quantitative way by measuring the pull on the ring when tipped by various amounts. The stirrup was bent so that the plane of the ring was not horizontal, and the difference in height between the two sides was measured with a cathetometer. From this the angle made between the plane of the ring and the horizontal was calculated. Ring Number 12 was used, and the data, which are given in the table below, are illustrated in Fig. 5.

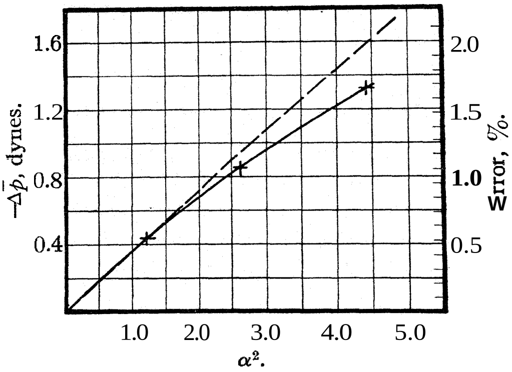

Fig. 5.—Error due to tipping of ring.

TABLE II

DATA WITH RING 12

Angle, α	α^2	P	Δp	Error, %
0.00	0.00	84.05	0.00	0.00
1.10	1.21	83.61	0.44	0.52
1.62	2.62	83.20	0.85	1.01
2.10	4.42	82.73	1.32	1.57

It is seen from the graph of the above data that for small angles such as are liable to be encountered in practice, the error introduced is proportional to the square of the angle. Δp is, therefore, expressed by the equation

$$-\Delta p = k\alpha^2$$

In the present case the equation holds for angles not greater than 1.5 degrees, and k has the value 0.36. From the graph it may be seen that for the error due to this source to be less than 0.1% the angle of tip must be less than 0.47 degree, and for an angle of 1 degree the error introduced is 0.43%.

The effect of the curvature of the meniscus and the size of the vessel was studied by making measurements of water contained in crystallizing dishes of various sizes. The crystallizing dish was placed on a glass desiccator triangle in a 2-liter beaker, and overflowed from the top, thus insuring uniformly clean surfaces. To prevent evaporation the top of the beaker was covered with a plate of glass in which a hole was bored. Measurements could not be made when the diameter of the dish was less than 7 cm., as the curvature of the meniscus was so great as to cause the ring to cling to the side of the dish. Ring Number 12 was used. The data are given in Table III.

TABLE III

OBSERVATIONS ON MENISCUS CURVATURE

Diam. of dish, cm.	7	8	9	10	12
P	83.96	84 03	84.08	84 05	84 06

While this effect is not great for dishes more than 7 cm. in diameter in the measurement of surface tension, it becomes of much greater importance in the measurement of interfacial tension.

The error caused by not having the wire all in the same plane cannot be measured quantitatively with any accuracy, but it was observed that this was an important source of error. This results in a consistently lower pull on the ring, and is one of the troublesome factors in measurements with the larger rings made of fine wire. In straightening the wire a small brass plate was used in which a groove was cut. The ring was set on the plate with the portion of the ring to be straightened across the groove, and then tapped gently with a small brass rod rounded at the end. While this method is not entirely satisfactory, it was the best of a number that were tried.

7. Method of Measurement of Surface Tension

The method of measurement was as follows. The flask was cleaned with hot cleaning solution (10 *cc.* of saturated potassium dichromate solution and 990 *cc.* of concd. sulfuric acid) and the solution was allowed to stand in the flask for fifteen minutes. The flask was then rinsed thoroughly with conductivity water. In the case of measurements on liquids other than water it was also dried by circulation of air, previously dried over sulfuric acid, and by gentle heating on the outside with a steam jet. The flask was then filled with the liquid (already at the temperature of the thermostat) to be measured and allowed to stand in the thermostat for three-quarters of an hour before measurements were made.

The ring was leveled as follows. It was suspended over a small gold plated brass table, fitted with leveling screws and polished to a mirror finish on top. The table was made level by a small right angle level, and the ring was lowered to within a half millimeter of the top of the table. By sighting between the top of the table and the ring in two mutually perpendicular directions, and by looking at the ring and its mirror image at the same time, considerably less then 30′ of tilt could be determined. The stirrup of the ring was bent until the plane of the ring appeared to be perfectly horizontal. It was then cleaned by heating to red heat in a flame. In the case of three or four of the rings in which the stirrups were silver soldered to the ring, the ring was cleaned by dipping into warm cleaning solution, rinsing thoroughly in conductivity water, and drying at some distance above a gas flame:

The flask was then put in position under the balance so that the plane of the inner cup was as nearly horizontal as possible. The ring was then connected with the fine aluminum rod from the left-hand stirrup of the balance beam by a jointed aluminum rod composed of links about two inches in length. On its end was a hook, the inner circumference of which was beveled to a knife edge to allow free motion of the stirrup loop over it. An inverted Erlenmeyer flask with a hole about 1 cm. in diameter blown in the bottom was placed in the top of the measuring flask to prevent evaporation.

The weight of the ring suspended in air was determined and taken as the zero weight. The cup in the flask was overflowed with plenty of liquid to insure a clean surface, and enough liquid withdrawn through the side-arm (A) (Fig. 3) to cause the liquid in the cup to become level instead of concave upward. With large rings the initial surface was made slightly convex upward, to such an extent that the outer part of the surface becomes plane when the ring is lifted to the height of detachment. The balance was lowered until the ring met the liquid, and then slowly raised while weights were added to determine the approximate maximum pull. In this procedure the addition of weights to the pan was made with the beam rest supporting the beam as in ordinary weighing, and during the addition of weight by the chain the rest was lowered only enough to allow the pointer to swing three divisions in either direction The final addition of weight and the raising of the balance were so regulated as to keep the pointer always at the scale zero. In check determinations the beam of the balance was raised and lowered again when the pull was about 10 mg. less than the maximum to insure its proper position, and the additional weight was added very slowly. When the maximum weight is reached, the balance pointer suddenly swings to the left and the liquid may or may not become detached from the ring, but any attempt to raise the balance---to bring the pointer back to zero--causes detachment of the liquid. The maximum weight was taken as the weight required to make the pointer suddenly move to the left, and which cannot be compensated by raising the balance without detachment of the liquid from the ring.

8. Experimental Results

The experimental results obtained by the ring method for water, benzene and bromobenzene are given in Tables IV, V and VI.

TABLE IV

WATER

Ring no.	M	p	V	R^3/V	γ/p
1	0.3446	64.89	0.3461	0.2055	1.1091
2	.5446	70.05	.5469	.4079	1.0274
3	.4451	68.04	.4470	.2973	1.0578
4	.7866	75.96	.7899	.6673	0.9475
5	1.0080	77.53	1.0123	1.0305	.9283
6	1.2196	78.08	1.2248	1.4771	.9218
7	1.2689	81.51	1.2743	1.4055	.8830
8	0.7374	85.00	0.7405	0.4185	.8467

TABLE IV *(Concluded)*

Ring no.	M	p	V	R^3/V	γ/p
9	0.4123	68.75	0.4140	0.2474	1.0468
10	.5950	72.91	.5975	.4318	0.9871
11	1.6040	82.08	1.6108	2.1996	.8768
12	1.9239	82.11	1.9320	3.1601	.8765
13	1.2853	84.92	1.2907	1.2749	.8475
14	0.7741	77.84	0.7774	0.6009	.9246
15	.9178	75.99	.9217	.9072	.9471
16	1.2435	76.97	1.2488	1.6030	.9350

TABLE V

BENZENE

Ring no.	M	p	V	R^3/V	γ/p
1	0.1514	28.51	0.1736	0.4096	0.9902
2	.2273	29.24	.2606	.8561	.9655
3	.1900	29.05	.2179	.6099	.9718
4	.3283	31.70	.3765	1.4000	.8905
5	.4180	32.15	.4793	2.1765	.8781
6	.5037	32.25	.5776	3.1320	.8754
7	.5306	34.09	.6084	2.9437	.8281
8	.3243	37.39	.3719	0.8333	.7550
9	.1804	30.09	.2069	.4949	.9392
10	.2515	30.82	.2884	.8946	.9160
11	.6699	34.28	.7682	4.6122	.8235
12	.8029	34.27	.9207	6.6312	.8238
13	.5465	36.11	.6267	2.6256	.7818
14	.3271	32.89	.3751	1.2452	.8538
15	.3768	31.20	.4321	1.9352	.9048
16	.5085	31.48	.5831	3.4332	.8968

TABLE VI

BROMOBENZENE

Ring no.	M	p	V	R^3/V	γ/p
1	0.1984	37.36	0.1333	0.5334	0.9569
2	.2939	37.80	.1976	1.1290	.9456
3	.2462	37.63	.1655	0.8030	.9500
4	.4255	41.09	.2861	1.8423	.8700
5	.5419	41.68	.3643	2.8635	.8577
6	.6534	41.83	.4393	4.1181	.8547
7	.6924	44.48	.4655	3.8474	.8037
8	.4291	49.47	.2885	1.0741	.7227
9	.2358	39.32	.1585	0.6461	.9092
10	.3265	40.01	.2195	1.1753	.8935
11	.8729	44.67	.5868	6.0380	.8003
12	1.0450	44.60	.7025	8.6909	.8016
13	0.7179	47.44	.4826	3.4096	.7536
14	.4269	42.93	.2870	1.6275	.8238
15	.4874	40.36	.3277	2.5517	.8858
16	.6583	40.75	.4426	4.5230	.8773

In the treatment of the results above the first problem was to find the variation of $\gamma/\mathbf{p}$ with R/r when R^3/V is kept constant at various values, so that the values of $\gamma/\mathbf{p}$ found experimentally could be converted into those of the closest even value of R/r. While the values could have been read from the $\gamma/\mathbf{p} - R^3/V$ plots of the values above, it was found that in the case of the smaller rings the curvature of the plot was so great that this could not be done accurately. Other functions were then resorted to

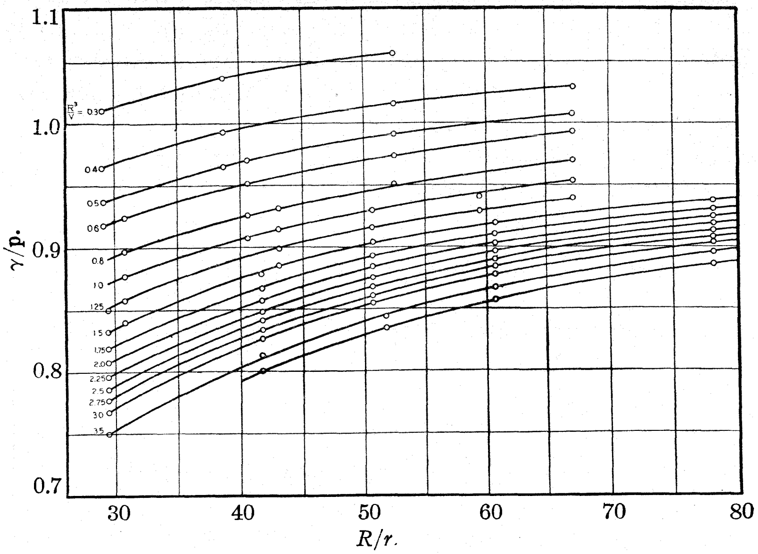

Fig. 6.—Correction curves for ring method.

TABLE VII
EXPERIMENTAL VALUES

Ring no.	Water R^3/V	Water $\gamma/\mathbf{p}$	Bromobenzene R^3/V	Bromobenzene $\gamma/\mathbf{p}$	Benzene R^3/V	Benzene $\gamma/\mathbf{p}$	R/r
1	0 2055	1 1116	0 5334	0 9569	0 4096	0 9932	40
2	.4079	1.0222	1.1290	9356	8561	.9555	60
3	.2973	1.0556	0 8030	9459	.6099	.9680	50
4	.6673	0 9408	1 8423	.8600	14000	.8810	40
5	1.0305	.9268	2 8635	.8557	2 1765	.8764	50
6	1 4771	.9208	4 1181	8532	3.1320	.8742	60
7	1.4055	.8785	3 8474	.7967	2 9437	.8217	40
9	02474	1.0496	0.6461	.9122	0.4949	.9412	30
10	,4318	0.9859	1 1753	8920	.8946	.9145	40
11	2.1996	.8725	6.0380	.7953	4 6122	.8185	50
12	3.1601	.8744	8.6909	7989	6 6312	.8211	60
13	1.2749	8504	3 4096	7570	2.6256	.7848	30
14	0.6009	.9216	1 6275	8288	1 2452	.8541	30
15	.9072	,9481	2 5517	.8869	1 9352	.9058	60
16	1.6030	.9368	4 523	.8773	3 4332	.8989	80

in order to reduce this inaccuracy. The values for rings with R^3/V between 0 and 1.0 were determined by plotting V/R^3 against $\gamma/\mathbf{p}$, and the values for rings with R^3/V values above 1.0 were determined by plotting log R^3/V against log $\gamma/\mathbf{p}$. In this way the curvature of the graphs was decreased to a minimum, and the accuracy greatly increased. When the resulting values of $\gamma/\mathbf{p}$ are plotted against R/r, the series of curves shown in Fig. 6 is obtained. The values of $\gamma/\mathbf{p}$ were then corrected to those of the closest value of R/r. These values are 30, 40, 50, 60 and 80. The corrected experimental values are given in Table VII.

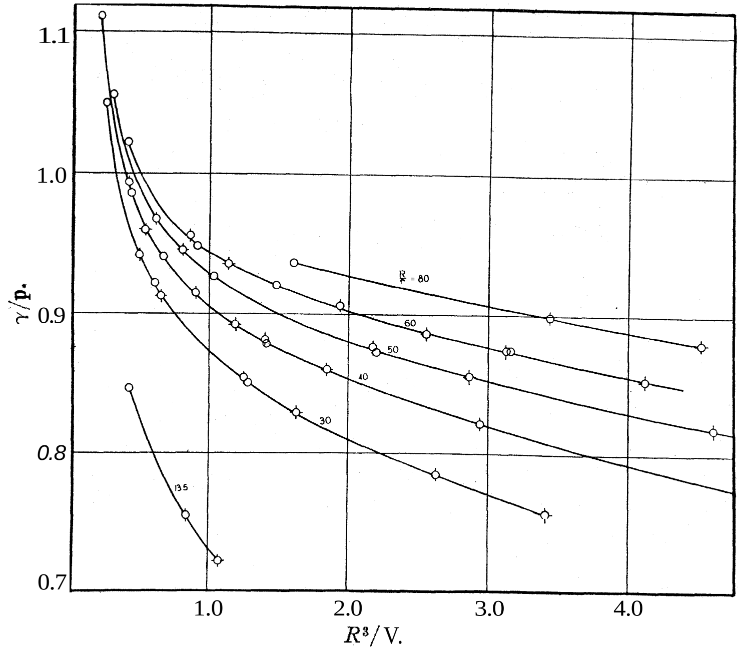

Fig. 7.—Correction curves for ring method.

The curves obtained by plotting the values above are shown in Fig. 7. Those obtained by plotting the values logarithmically are shown in Fig. 8. It is seen that the curvature is greatly reduced by plotting the values in the latter way. By use of the $\gamma/\mathbf{p} - R/r$ graphs, curves were also obtained for intermediate values of R/r, from which were read the values that compose the table mentioned in the following section.

9. Ring Method Correction (F) for the Shapes of the Surfaces

In order to avoid the necessity of plotting the corrected experimental values for use in actual work, a table was constructed for a number of intermediate values of R/r as well as the even values. The values of $\gamma/\mathbf{p}$ given in the tables for R/r (except for too low values of R^3/V) equal to 30, 40, 50, 60 and 80 are considered accurate to 0.3% with a probable error of less than 0.2%, while those for the intermediate values of R/r are considered accurate to 0.4% with a probable error of less than 0.3%. The values are given in Table VIII.

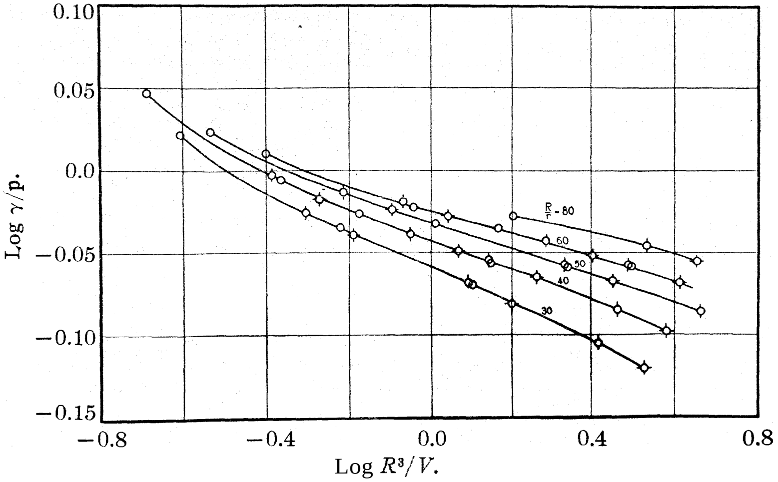

Fig. 8.—Correction curves for ring method.

10. Weights of the Residual Drops on the Rings

There has been a discussion concerning the importance of the drops of liquid which adhere to the ring after it has been pulled out of the liquid. Klopsteg[7] suggested that the zero weight should be taken at the weight of the ring plus the weight of the drops of liquid which adhere to it, while MacDougall[8] considers that such a correction is not justified. As a result manufacturers have printed instructions that in the use of their apparatus the intial reading be taken at the weight of the ring in air plus the weight of the adhering drops, and suggest that additional accuracy is acquired. Since, as may be seen from the experimental data presented in this paper, most of the values for surface tension (p) obtained by the

TABLE VIIIA

CORRECTION FACTORS FOR EVEN VALUES OF R/r

R^3/V	γ/p or F R/r = 30	γ/p or F R/r = 40	R^3V	γ/p or F R/r = 30	γ/p or F R/r = 40
0.20	...	1.119	0.26	1.048	1.070
.21	...	1.108	.26	1.039	1.063
.22	...	1.097	.27	1.031	1.056
.23	...	1.087	.281	1.025	1.050
.24	1.056	1.078	.29	1.018	1.043

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[7] Klopsteg, Science, 60, 319 (1924).

[8] MacDougall, *ibid.*, [N. S.] **62**, 290 (1925).

TABLE VIIIB

CORRECTION FACTORS (F) FOR THE RING METHOD

R^3/V	$R/4$ = 30	32	34	36	38	40	42	44	46	48	50	R/r = 52	54	56	58	60
0.30	1.012	1.018	1.024	1.029	1.034	1.038	1.042	1.046	1.049	1.052	1.054					
.31	1.006	1.013	1.018	1.024	1.028	1.033	1.039	1.041	1.044	1.046	1.049					
.32	1.001	1.008	1.012	1.019	1.023	1.028	1.033	1.035	1.039	1.041	1.045					
.33	0.9959	1.003	1.008	1.014	1.018	1.024	1.028	1.030	1.035	1.036	1.040					
.34	.9913	0.998	1.003	1.010	1.014	1.019	1.023	1.026	1.031	1.032	1.036					
.35	.9865	.993	0.999	1.006	1.008	1.015	1.019	1.022	1.026	1.027	1.031					
.36	.9824	.989	.995	1.002	1.005	1.010	1.015	1.018	1.022	1.024	1.027					
.37	.9781	.985	.991	0.998	1.001	1.006	1.011	1.014	1.018	1.020	1.024					
.38	.9743	.981	.987	.995	0.998	1.003	1.007	1.010	1.015	1.017	1.020					
.39	.9707	.977	.983	.991	.994	0.9988	1.004	1.007	1.011	1.013	1.017					
.40	.9672	.974	.980	.986	.991	.9959	1.000	1.004	1.008	1.010	1.013	1.016	1.018	1.020	1.021	1.022
.41	.9636	.970	.976	.983	.987	.9922	0.997	1.001	1.005	1.007	1.010	1.013	1.015	1.017	1.019	1.019
.42	.9605	.968	.973	.980	.984	.9892	.994	0.998	1.002	1.004	1.007	1.010	1.013	1.014	1.016	1.017
.43	.9577	.964	.970	.977	.981	.9863	.991	.995	.999	1.001	1.005	1.007	1.010	1.011	1.014	1.014
.44	.9546	.961	.967	.974	.979	.9833	.988	.992	.997	0.998	1.002	1.005	1.007	1.009	1.011	1.011
.45	.9521	.959	.965	.971	.976	.9809	.986	.990	.993	.996	0.9993	1.002	1.004	1.006	1.009	1.009
.46	.9491	.956	.962	.969	.973	.9779	.983	.987	.991	.994	.9968	1.000	1.002	1.004	1.006	1.007
.47	.9467	.954	.960	.966	.971	.9757	.980	.985	.988	.992	.9945	0.998	1.000	1.002	1.004	1.005
.48	.9443	.951	.957	.963	.968	.9732	.978	.983	.986	.989	.9922	.995	0.997	0.999	1.002	1.003
.49	.9419	.949	.955	.961	.966	.9710	.976	.981	.984	.987	.9899	.993	.995	.997	1.000	1.001

TABLE VIIIC

CORRECTION FACTORS (F) FOR THE RING METHOD

R^3/V	$R/r = 30$	32	34	36	38	40	42	44	46	48	50	52	54	56	58	60
0.50	0.9402	0.946	0.952	0.959	0.964	0.9687	0.973	0.978	0.981	0.985	0.9876	0.991	0.993	0.995	0.997	0.9984
.51	.9378	.944	.950	.956	.961	.9665	.971	.976	.979	.983	.9856	.989	.991	.993	.995	.9965
.52	.9354	.942	.948	.954	.959	.9645	.969	.974	.977	.981	.9836	.987	.989	.991	.994	.9945
.53	.9337	.940	.946	.952	.957	.9625	.967	.972	.975	.979	.9815	.985	.987	.990	.992	.9929
.54	.9315	.938	.944	.950	.955	.9603	.965	.970	.974	.977	.9797	.983	.986	.988	.990	.9909
.55	.9298	.936	.942	.948	.953	.9585	.964	.968	.972	.975	.9779	.981	.984	.986	.988	.9892
.56	.9281	.934	.940	.946	.951	.9567	.962	.966	.970	.974	.9763	.980	.982	.984	.986	.9879
.57	.9262	.932	.939	.944	.949	.9550	.960	.964	.968	.972	.9745	.978	.980	.983	.984	.9861
.58	.9247	.930	.938	.942	.947	.9532	.958	.963	.966	.970	.9730	.976	.979	.981	.982	.9842
.59	.9230	.929	.935	.940	.946	.9515	.956	.961	.965	.968	.9714	.975	.977	.979	.981	.9827
.60	.9215	.927	.933	.939	.944	.9497	.954	.959	.963	.967	.9701	.973	.976	.978	.979	.9813
.62	.9184	.924	.930	.936	.041	.9467	.951	.956	.960	.964	.9669	.970	.973	.975	.976	.9784
.64	.9150	.921	.927	.932	.938	.9439	.948	.953	.957	.961	.9643	.968	.970	.972	.973	.9754
.66	.9121	.918	.925	.930	.935	.9408	.946	.950	.954	.959	.9614	.965	.967	.969	.971	.9728
.68	.9093	.915	.921	.927	.932	.9382	.943	.948	.951	.956	.9590	.963	.965	.967	.968	.9703
.70	.9064	.912	.919	.924	.929	.9352	.940	.945	.949	.953	.9563	.960	.962	.964	.966	.9678
.72	.9037	.910	.916	.921	.927	.9328	.937	.943	.946	.951	.9542	.957	.960	.962	.964	.9656
.74	.9012	.907	.913	.919	.924	.9303	.935	.940	.944	.949	.9519	.955	.958	.960	.962	.9636
.76	.8987	.905	.911	.916	.922	.9277	.933	.938	.942	.947	.9459	.953	.956	.958	.860	.9616
.78	.8964	.902	.908	.914	.920	.9258	.930	.936	.939	.944	.9475	.951	.954	.956	.958	.9598

TABLE VIIID

CORRECTION FACTORS (F) FOR THE RING METHOD

R^3/V	R/r = 30	32	34	36	38	40	42	44	46	48	50	52	54	56	58	60
0.80	0.8937	0.900	0.906	0.912	0.918	0.9230	0.928	0.933	0.937	0.942	0.9454	0.949	0.952	0.954	0.956	0.9581
.82	.8917	.898	.904	.909	.915	.9211	.926	.931	.935	.940	.9436	.947	.950	.952	.954	.9563
.84	.8894	.895	.902	.907	.913	.9190	.924	.929	.933	.938	.9419	.946	.949	.951	.953	.9548
.86	.8874	.893	.900	.905	.911	.9171	.922	.927	.932	.936	.9402	.944	.947	.949	.951	.9534
.88	.8853	.891	.898	.903	.909	.9152	.921	.926	.930	.934	.9384	.942	.945	.947	.950	.9517
.90	.8831	.889	.896	.902	.907	.9131	.919	.924	.928	.933	.9367	.940	.943	.946	.948	.9504
.92	.8809	.887	.894	.900	.905	.9114	.917	.922	.926	.931	.9350	.939	.942	.945	.947	.9489
.94	.8791	.885	.892	.898	.904	.9097	.915	.920	.925	.929	.9333	.937	.940	.943	.945	.9476
.96	.8770	.883	.890	.896	.902	.9074	.914	.919	.923	.928	.9320	.936	.939	.942	.944	.9462
.98	.8754	.882	.888	.894	.900	.9064	.912	.917	.922	.926	.9305	.934	.937	.940	.943	.9452
1.00	.8734	.880	.886	.892	.899	.9047	.910	.916	.920	.925	.9290	.933	.936	.939	.941	.9438
1.05	.8688	.875	.882	.888	.895	.9007	.906	.912	.916	.921	.9253	.929	.932	.936	.938	.9408
1.10	.8644	.871	.878	.885	.891	.8970	.903	.908	.913	.917	.9217	.925	.929	.933	.935	.9378
1.15	.8602	.867	.875	.881	.888	.8937	.900	.905	.910	.914	.9183	.922	.926	.930	.933	.9352
1.20	.8561	.864	.871	.878	.885	.8904	.897	.902	.907	.911	.9154	.920	.923	.927	.930	.9324
1.25	.8521	.860	.868	.875	.882	.8874	.893	.899	.904	.908	.9125	.916	.920	.924	.927	.9300
1.30	.8484	.856	.864	.871	.879	.8845	.891	.896	.901	.905	.9097	.914	.917	.921	.925	.9277
1.35	.8451	.853	.861	.869	.876	.8819	.888	.893	.898	.903	.9068	.911	.915	.919	.922	.9253
1.40	.8420	.850	.858	.866	.873	.8794	.885	.891	.896	.900	.9043	.909	.913	.916	.920	.9232
1.45	.8387	.847	.855	.863	.871	.8764	.883	.888	.893	.898	.9014	.906	.910	.914	.918	.9207

TABLE VIIIE

CORRECTION FACTORS (F) FOR THE KING METHOD

R^3/V	R/r = 30	32	34	36	38	40	42	44	46	48
1.50	0.8356	0.844	0,853	0.861	0.868	0.8744	0.881	0.886	0.891	0.895
1.55	.8327	.841	.850	.858	.866	.8722	.878	.883	.888	.893
1.60	.8297	.839	.848	.856	.863	.8700	.876	.881	.886	.891
1.65	.8272	.836	,845	.853	.861	.8678	.874	.879	.884	.889
1.70	.8245	.834	.843	.851	.859	.8658	.872	.877	.882	.886
1.75	.8217	.831	.840	.849	.857	.8638	.870	.875	.880	.884
1.80	.8194	.829	.838	.847	.855	.8618	.868	.873	.878	.882
1.85	.8168	.827	.836	.845	.853	.8596	.866	.871	.876	.881
1.90	.8143	.824	.834	.943	.851	.8578	.864	.869	.874	.879
1.95	.8119	.822	,832	.841	.849	.8559	.862	.867	.872	.877
2.00	.8098	.820	.830	.839	.847	.8539	.860	.865	.870	.875
2.10	.8056	.816	.826	.835	.843	.8502	.856	.862	.867	.872
2.20	.8015	.812	.822	.831	.839	.8464	.853	.858	.864	.869
2.30	.7976	.808	.818	.828	.835	.8428	,849	.855	.861	.866
2.40	.7936	.804	.814	.824	.832	.8393	.846	.852	.857	.863
2.50	.7898	.800	.811	.820	.828	.8360	.843	.849	.854	.860
2.60	.7861	.797	.807	.817	.825	.8325	.840	.846	.851	.857
2.70	.7824	.793	.803	.813	.822	.8291	.836	.843	.848	.854
2.80	.7788	.790	.800	,810	.818	.8260	.834	.840	.846	.852
2.90	.7752	.786	.796	.806	.815	.8230	.831	.837	.843	.849
3.00	.7716	.783	,793	.803	.812	.8200	.828	.834	.841	.846
3.10	.7677	.779	,790	.800	.809	.8170	.825	.832	.838	.844
3.20	.7644	.776	.787	.797	.806	.8140	.822	.829	.835	.842
3.30	.7610	.772	.783	.793	,803	.8113	.820	.827	.833	.840
3.40	.7572	.769	.780	.790	.800	.8083	.817	.824	.831	.837
3.50	.7542	,766	.777	.788	.798	.8057	.814	.822	.829	.835

R^3/V	50	52	54	56	58	60	65	70	75	80
1.50	0.8995	0.904	0.908	0.912	0.916	0.9190	...	...	...	...
1.55	.8970	.901	.906	.910	.914	.9171	...	...	...	0.9382
1.60	.8947	.899	.904	.908	.912	.9152	0.922	0.928	0.933	.9365
1.65	.8927	.897	.902	.906	.910	.9133	.921	.927	.931	.9354
1.70	.8906	.895	.900	.904	.909	.9116	.919	.925	.930	.9341
1.75	.8886	.893	.898	.902	.907	.9097	.918	.924	.929	.9328
1.80	.8867	,891	.896	.900	.905	.9080	.916	.922	.927	.9317
1.85	.8849	.889	.895	.899	.903	.9066	.915	.921	.926	.9305
1.90	.8831	.888	.893	.897	.902	.9047	.913	.919	.925	.9291
1.95	.8815	.886	.891	.895	.900	.9034	.912	.918	.923	9281
2.00	.8798	.884	.890	.893	.899	.9016	.910	.917	.922	.9270
2.10	.8768	.881	.886	.890	.895	.8991	.908	.914	.920	.9247
2.20	.8738	.879	.883	.887	.892	.8962	,905	.911	.917	.9226
2.30	.8710	.876	.880	.884	.890	.8935	.903	.909	.915	.9206
2.40	.8680	.873	.878	.882	.887	.8910	.900	.907	.913	.9185
2.50	.8651	.870	.875	.879	.884	.8884	.898	.904	.910	.9166
2.60	.8624	.868	.872	.877	.882	.8859	.895	.902	.908	.9145
2.70	.8598	.865	.870	.874	.880	.8837	.893	.900	.906	.9126
2.80	.8570	.862	.867	.872	.877	.8813	.891	.898	.904	.9107
2.90	.8545	.860	.865	.870	.875	.8790	.889	.896	.902	.9089
3.00	.8521	.858	.863	.868	.873	.8770	.887	.894	.900	.9068

TABLE VIIIE (*Concluded*)

R^3/V	50	52	54	56	58	60	65	70	75	80
3.10	0.8494	0.855	0.860	0.866	0.871	0.8750	0.885	0.892	0.899	0.9049
3.20	.8472	.853	.858	.864	.869	.8730	.883	.890	.897	.9030
3.30	.8449	.851	.856	.862	.866	.8710	.881	.888	.895	.9012
3.40	.8424	.849	.854	.860	.864	.8688	.879	.886	.893	.8993
3.50	.8404	.847	.852	.858	.862	.8668	.877	.884	.892	.8974

pseudo-ring method are too high, the values seem to be improved, but this is done only by introducing a second error. The theory indicates that the zero point should be taken at the weight of the dry ring in air. The weight of liquid which adheres to one of our rings is constant if the air is saturated with vapor, and values of the weights of liquid which adhere to some of the rings are given in Table IX.

TABLE IX

WEIGHT OF RESIDUAL DROPS

Ring no.	Water	Benzene	Ring no.	Water	Benzene
2	0.0013	......	8	....	0.0033
3	.0015	......	9	0.0018	.0009
5	.0033	......	10	.0167	.0019
6	.0044	......	11	....	.0044
7	.0081	......	14	.0155	.0029

11. The Variation of the Pull on the Ring with the Height of the Ring above the Free Liquid Surface

Dorsey[9] has recently suggested that many workers, particularly those using the DuNoüy tensiometer, might be measuring the pull of a film of liquid upon the ring rather than the maximum pull of the liquid. It was therefore considered important to study the variation of the pull on the ring with the distance it is raised above the free surface of the liquid. The values, which are shown graphically in Fig. 9, are given in Table X. Ring 10 was used.

TABLE X

RESULTS

Pull in grams	Height in cm.	Pull in grams	Height in cm.
0.3064	0.062	0.5894	0.290
.4064	.120	.5909	.300
.4564	.151	Maximum = 0.5912	...
.5064	.186	0.5898 to 0.5899	.305
.5264	.203	.5836 to .5895	.319
.5464	.223	.5823 to .5875	.324
.5664	.248	.5730 to .5839	.338
.5764	.262	.5616 to .5712	.352
.5864	.279	.5425 to .5606	.365
.5884	.287	.5066 to ...	.380, height at detachment

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[9] Dorsey, *Science,* 69, 187 (1929).

It is evident that as the ring is pulled out of the liquid the pull on it increases to a maximum and then decreases.

It is at once evident that there is no danger of measuring any other than the maximum pull with the balance with the technique used, since great difficulty was experienced in measuring points beyond the maximum. After the maximum pull had been reached, the balance pointer swung to the left and could be made to return only by decreasing the weight by fifteen or twenty milligrams, when it would swing quickly to the right and remain there. During this time its motion was restricted by the beam rest to one division in either direction from the scale zero. In order to make any measurements of even low precision beyond the maximum it was necessary to attach a stop which would allow the pointer to swing from zero to a point one-half scale division away in one direction at a time. The weight that would just suffice to make the pointer leave zero in one direction and then the weight to make it leave in the other direction were determined. In this way the limits of the pull on the ring were determined for the heights above the height of maximum pull.

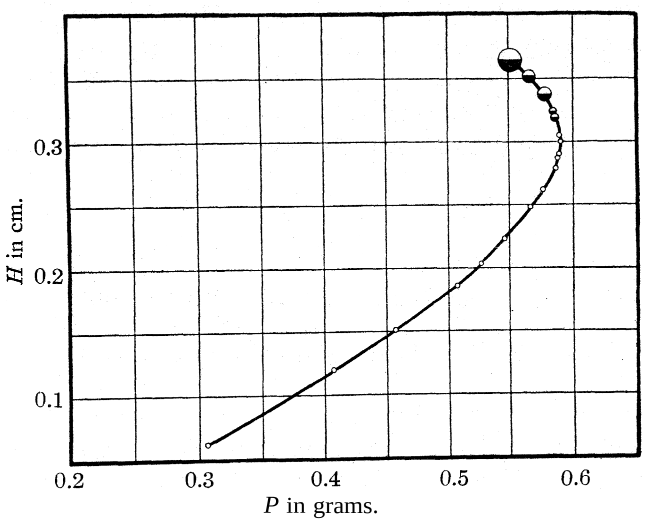

Fig. 9.—Variation of pressure with height of ring.

It was noticed, particularly in the case of the smaller rings, that the liquid column had a tendency to adhere to the ring and be pulled out into a film after the pointer had swung to the left, signifying that the maximum pull had been reached. If, however, the beam rest is further released from under the balance beam the liquid breaks. Until the maximum pull is reached the edge of the liquid meniscus appears to be attached to the ring.

12. Preliminary Application of the Ring Method to Interfacial Tension

Measurements of the interfacial tension between water and benzene were also made in order to see whether the ring method is a practical one for such measurements.

The general method of measurement was the same as for surface tension with only slight modifications. The measurements were carried out in a 2-liter Erlenmeyer flask provided with a special long neck. The ring was connected with the aluminum rod running up to the balance beam by means of a length of platinum wire 0.1 mm. in diameter. This was quite fine, in order to reduce the effect of surface forces and the effect of buoyancy. The layer of benzene was several centimeters deep, so that the ring and its stirrups were completely immersed throughout the measurements. The initial weight was the weight of the ring completely immersed in benzene. The results obtained with Rings 7 and 5 are given in Table XI. The interfacial tension is calculated by use of the correction factors (F).

TABLE XI

RESULTS

King	M	P	V	R^3/V	γ/p	γ
7	0 5345	34.33	4 335	0.4132	0 995	34.16
5	.4190	32 23	3 398	.3070	1.051	33.91

t, 25°; $(D - d) = 0.1233$; γ by the drop weight–volume method, 34.71.

On account of the steepness of the correction curves in this region, better results could probably be obtained with larger rings (of as small or smaller wire).

In the ring method the angle of contact between the interface and the ring must be zero, a condition which is more difficult to meet, in general, with interfacial than with surface tension.

There are probably a number of additional factors to be considered in the measurement of interfacial tension by the ring method, but the deviations from the standard value are not greater than is to be expected from the first preliminary determinations.

Measurements were also made with smaller rings and the values of γ/p

TABLE XII

DATA

Ring	M	p	V	R^3/V	γ/p
1	0.1272	23.95	1.032	0.0689	1.449
2	.2103	27.05	1.706	.1308	1.283
3	.1680	25.68	1.363	.0997	1.352
4	.3120	30.13	2.530	.2083	1.134
9	.1513	25.23	1.227	.0835	1.376
10	.2281	27.95	1.850	.1395	1.242

γ, 34.71; $(D - d) = 0.1233$.

were calculated by assuming that the interfacial tension measured had the standard value. The purpose of this was to show the magnitude of the error that may be introduced by neglect of the correction factors. The data are given in Table XII.

It is seen that as high as 45% error may be incurred by this neglect in the measurement by the use of a moderately small ring, since R^3/V is very small, and the curvature in this region of the curve is very great. The neglect of the correction with the ring furnished with the Cenco Tensiometer gives results which are 20% too low, which accounts for the extremely inaccurate results which have been obtained in the measurement of interfacial tension by the "ring method."

Summary

1. Until three years ago there was no *ring method* for the *measurement* of surface tension, since, in general, all that was determined was the pull on a ring, and this pull was incorrectly assumed to be equal to the surface tension multiplied by twice the mean circumference of the ring. Even in cases in which attempts were made to use the incomplete theory of the ring method, it was found that rings of the dimensions required by the theory were incapable of use. Three years ago Harkins, Young and Cheng applied the principle of similitude to this problem, and determined the values of the function F in the correct equation

$$\gamma = \frac{Mg}{4\pi R} \times f(R^3/V, R/r) = \frac{Mg}{4R} F$$

In this paper a larger number of values of F, determined to a higher degree of accuracy, are given. These were obtained by determining the values of the maximum pull ($P = Mg$) for sixteen rings with radii from 0.4 to 0.8 cm. made from wire with radii between 0.009 and 0.05 cm. and with values of R/r between 13.9 and 78.3.

2. The values of the maximum pull were determined for three liquids: water, benzene and bromobenzene. Accurate determinations of the surface tension by the capillary height method gave for the liquids used 28.23 dynes per cm. for benzene and 35.75 for bromobenzene at 25°.

3. Various sources of error in the experimental methods were investigated. (a) The error introduced when the plane of the ring is not horizontal is proportional to the square of the angle of tip when the angle is small. An angle of 0.4 degree causes an error of 0.1% and 1.0 degree of 0.45%. (b) The diameter of the vessel which confines the surface of the liquid should be not less than 8 cm. (c) An error is introduced if the ring does not lie in a plane.

4. An apparatus for the accurate determination of surface tension by the ring method is described. This consists of a chainomatic balance, supported by a machine which raises or lowers it with a minimum amount

of vibration, and a special flask, designed to give a clean liquid surface, buried under the water of a thermostat.

5. It was found that the accuracy of measurement of the dimensions of the rings depends greatly upon the method of illumination employed, and apparatus for these measurements was developed.

6. It was shown that at a certain height above the surface of the liquid the pull on the ring reaches a maximum. This maximum pull is what was determined in the measurements reported.

7. A necessary condition of the ring method is that the angle of contact between the ring and the liquid be zero.

8. Preliminary measurements indicate that the ring method may be used for the determination of interfacial tension.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND FROM ARMOUR INSTITUTE OF TECHNOLOGY]

A THEORY OF THE RING METHOD FOR THE DETERMINATION OF SURFACE TENSION

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The most convenient method for the determination of surface tension is perhaps what is known as the ring method. It has been used extensively, for example, by DuNoüy[1] in the case of numerous biological liquids. It is convenient because the experimental procedure necessary to obtain a fair degree of accuracy can be made very simple, although of course it becomes much more complicated when a higher degree of accuracy is sought. The essentials of the procedure are a ring, capable of being wetted by the liquid whose surface tension is to be measured, suspended horizontally in the flat surface of that liquid, and some device to measure the force necessary to separate ring and liquid. That the applied force may be changed gradually, a torsion balance is often used but a beam balance of the chainomatic type is also satisfactory. From this measured force, expressed as a weight, a quantity which many assume to be the value of the surface tension is often obtained from the relationship

$$W = 4\pi R\gamma \qquad (1)$$

where R is the radius of the ring, γ the surface tension and W the maximum weight of liquid held up or the pull on the ring at the instant of rupture. Modifications have been introduced into this equation, such as the substitution of $(R_1 + R_2)/2$ for r, where R_1 and R_2 are the inner and outer radii of the ring. But the validity of this relationship is not at all obvious. An experimental study of it by Harkins, Young and Cheng[2] and

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[1] DuNoüy, *J. Gen. Physiol.*, 1, 521 (1918–1919), etc.

[2] Harkins, Young and Cheng, Science, 64, 93 (1926).

a later one by Harkins and Jordan[3] indicate that it is in error in some cases by as much as 30% in either direction, plus or minus. The experiments of Harkins and his collaborators are expressed in the form of a series of empirical curves which involve the value of the surface tension as determined by a so-called absolute procedure and which must be used to correct the value given by the above relationship. It should be noted in this connection that a precisely analogous correction for the drop weight procedure for measuring surface tension was proposed by Harkins and Brown.[4] The purpose of this paper is to establish a theoretical basis for these empirical correction curves to the ring procedure, so that the values of surface tension as thus obtained may be accepted with that additional confidence which is given to a procedure based on a solid theoretical foundation. A similar study of the theoretical basis for the corrections to be used with the drop weight procedure made by Freud and Harkins[5] should be consulted for certain details of the mathematical analysis. These two studies are interrelated.

The ring method, and for that matter many other methods for the determination of surface tension, depends upon the equilibrium forms assumed by liquid surfaces under the combined action of their own surface tension and some external forces, of which gravity usually is the dominant one. The capillary rise method is usually considered an absolute procedure largely because it is affected by the shape of the liquid surface less than any of the others. In this procedure it enters only as a correction in estimating the volume of liquid in the meniscus. The shapes taken by liquid surfaces play a much more significant role in the bubble pressure, sessile drop, hanging drop and drop weight procedures, none of which accordingly have been regarded as fundamental. As was indicated in our study of the shapes of hanging and of detaching drops, the drop weight procedure alone of those just mentioned involves the properties of a dynamic system, the others being stable even though some of them are at the very limit of stability. It is only in drop weight procedure that the theory is not complete; in this case the weight of the detached drop involves changes in the shape of the drop during the process of detachment, which, of course, cannot be explained by any theory of static liquid surfaces. A dynamic theory has been proposed by us[5] but it proved much too complicated to be applied. The ring procedure, as this paper shows, is another that may be adequately based on sound theory. There is no fundamental reason why it too should not be regarded as an absolute method.

A fundamental equation for the shapes of liquid surfaces, credited to Laplace, is

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[3] Harkins and Jordan, THIS JOURNAL, 52, 1751 (1930).

[4] Harkins and Brown, *ibid.*, 38, 246–252 (1916).

[5] Freud and Harkins, *J. Phys. Chem.*, 33, 1217–1234 (1929).

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{P}{\gamma} \qquad (2)$$

where P is the pressure and R_1 and R_2 are the two principal radii of curvature at any point in the surface. For $1/R_1$ and $1/R_2$ may be substituted their equivalents, $\mathrm{d}u/\mathrm{d}x$ and u/x, in the special case of liquid surfaces of revolution. Here x is the horizontal distance of the point from the axis of symmetry, and u is the sine of the angle which the tangent to the surface at the point makes with the x-axis. The latter is, in the notation of this paper, coincident with the level of the undisturbed surface of the liquid. For P may be substituted $\pm ygd$, the sign depending upon the particular surface involved. P is really a composite of several factors such as barometric pressure, gas pressure, head of liquid above the point and possibly others. All, however, may be included in the term ygd if the x-axis is taken at what may be termed the "ideal level" of the surface, and y is the vertical distance of the point from this level. The question of the proper sign for these terms is important. It has been found convenient, in this paper, to hold the convention that R_1 and R_2 are positive when the osculatory circle is on the liquid side of the surface, and negative when on the gaseous side. This usually can be determined by inspection. $\mathrm{d}u/\mathrm{d}x$ and u/x are numerically equal to $1/R_1$ and $1/R_2$ but are like them in signs only when the original choice of u or v, the cosine of the angle of which u is the sine, is such as to make them so. The signs of $\mathrm{d}u/\mathrm{d}x$ and u/x can also be told by inspection. If they do not agree with those of $1/R_1$ and $1/R_2$, this fact must be formulated by preceding $\mathrm{d}u/\mathrm{d}x$ and u/x, in the equation, with negative signs. The sign of the ygd term also can be told by inspection. It depends upon whether the "ideal level" is above or below the point in question. If the effect of the weight of the column of liquid is a push on the surface from the liquid side, the absolute value of the weight is positive; if it is a pull, the absolute value is to be given the negative sign. For the quantity gd/γ may be substituted its equal by definition, $2/a^2$, where a^2 is the capillary constant of the liquid; and a^2 may be eliminated by the device of changing the variables from x and y to $a\bar{x}$ and $a\bar{y}$, thus eliminating all characteristics of any particular liquid. The equation in this form becomes

$$\frac{\mathrm{d}u}{\mathrm{d}\bar{x}} + \frac{u}{\bar{x}} = \pm 2\bar{y} \qquad (3)$$

This equation describes the surfaces of a very diverse set of phenomena: pendent drops, drops of fluid in a medium of greater density on a tip pointing upward, menisci, both convex and concave, the surface of a liquid surrounding a vertical rod whether or not the rod is wetted, the liquid surface raised by a disk, bubbles of a fluid in a heavier medium on a tip pointing downward, and sessile drops—in fact all liquid surfaces of revolution. The fact that this equation applies only to surfaces of revolution excludes its application to such forms, for example as are produced when a wetted rectangular plate is raised from the surface of a liquid.

The ring method involves two of these shapes, the meniscus and the surface raised by a disk. Shapes of menisci are not too difficult to obtain. They are determined by mechanical integration of the equation exactly as described in our previous study of hanging drops, with the difference that if u is considered positive, increasing from 0 to 1 as $\bar{x}$ increases from 0, $\bar{y}$ must be considered negative in the equation, as $du/d\bar{x}$ and $u/\bar{x}$ do not agree in sign with $1/R_1$ and $1/R_2$, and the weight of the liquid causes a pull on the surface. The tables of Bashforth and Adams[6] give the data for a few of the menisci in Fig. 1. Unfortunately these tables do not include data for menisci for which ? at the y-axis is smaller than 0.1414. The numerical integration is exactly as originally described by Lohnstein,[7] with the change in sign mentioned above.

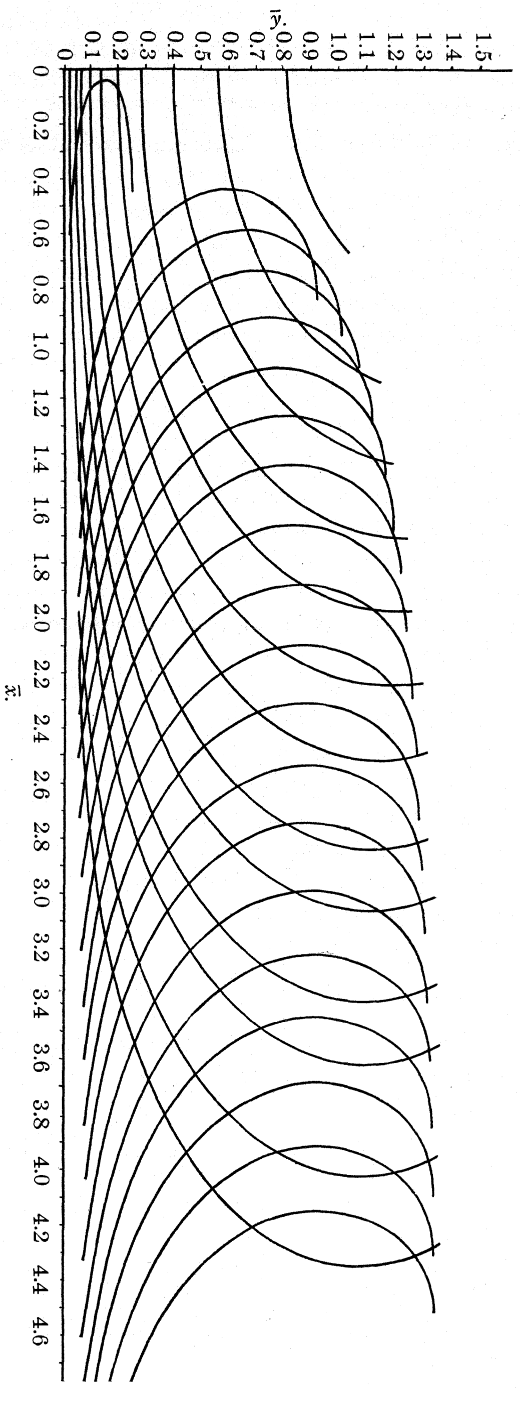

Fig. 1.—Meniscus and disk curves. Expansion of $du/d\bar{x} + u/\bar{x} = \pm 2\bar{y}$.

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[6] Bashforth and Adams, "Attempt to Test Theories of Capillary Action," Cambridge University Press, 1888.

[7] Lohnstein, *Ann. Physik*, [4] **20,237**, 606 (1906).

In the case of the outside surface sloping away from the ring, however, the problem is less simple. It must be recalled that this equation cannot be integrated, and even mechanical integration requires that $\bar{x}$, $\bar{y}$ and u be known for some particular point in the surface. In the cases of a stable pendent drop and a meniscus, it is known that at the very bottom u equals zero because at this point the tangent to the surface is parallel to the Z-axis, and $\bar{x}$ and $\bar{y}$ may be known from a suitable choice of the coordinate system. In the case of the surface raised by a disk, however, no point is really known except at infinite distance from the disk, that is, in the undisturbed level of the surface. Here $\bar{x} = \infty$, $\bar{y} = 0$ and $u = 0$. Because one of the coördinates of this known point has the value of infinity, the method of numerical integration, using Taylor's theorem, is inapplicable. However, we also know that $\bar{y}$ and u become very nearly equal to zero before $\bar{x}$ becomes very large. We have considered it sufficiently precise to assume that $\bar{y}$ and u become equal to 0.00001 units at distances from the axis of symmetry varying from 7.5 to 12.0 units. These distances were chosen because the resulting curves lay in the region experimentally investigated by Harkins and his collaborators. One curve starting much closer to the y-axis is given, but was not used in any of the calculations. This approximation involves an error so small that conclusions can nevertheless be made with a precision quite equal to that given by the best experimental technique.

It will be observed that our choice makes the sign of u positive for these outside surfaces, and thus fixes the signs to be used in Equation **3.** As $\bar{y}$ and u both increase with decreasing $\bar{x}$, the tangents u/v and $du/d\bar{x}$ are both negative, thus making v also negative; $u/\bar{x}$ is positive. Inspection shows that $1/\bar{R}_1$ is negative and $1/\bar{R}_2$ is positive according to our convention. Since these agree in sign with $du/d\bar{x}$ and $u/\bar{x}$, and the weight of the liquid column causes a pull on the surface, the equation to be used for these outside surfaces, thus, is

$$\frac{du}{d\bar{x}} + \frac{u}{\bar{x}} = -2\bar{y} \tag{4}$$

Had a negative sign been chosen for u, $d\bar{y}/d\bar{x}$ and $u/\bar{x}$ would have been negative and $du/d\bar{x}$ and v positive. In this case $du/d\bar{x}$ and $u/\bar{x}$ do not agree in sign with $1/\bar{R}_1$ and $1/\bar{R}_2$, so the equation would have been

$$-\frac{du}{d\bar{x}} - \frac{u}{\bar{x}} = -2\bar{y}, \text{ or} \tag{5}$$

$$\frac{du}{d\bar{x}} + \frac{u}{\bar{x}} = 2\bar{y} \tag{5'}$$

Mechanical integration of Equations 4 and 5 gives the same curve.

The two families of surfaces obtained in these ways are given in Pig. 1. The left edge of the figure, the y-axis, is the axis of symmetry, and the lower edge, the Z-axis, is the level of the undisturbed liquid. The family of curves crossing the axis of symmetry represents the shapes of the menisci obtained with various rings for the different heights to which they are raised above the surface. The family reaching apparently to infinity at the right edge of the figure represents the shapes of the outside surfaces formed by the raised rings. If a ring made of wire with a rectangular cross section, one of whose edges is in the plane of the ring, is lifted from the Z-axis in such a way that its lower edge alone is wetted, the plane of the ring remaining parallel to the flat surface of the liquid, the various portions of the family of meniscus curves intersected by the lower left corner of the wire give the shapes of the crater-like formations at the center of the raised liquids. Similarly, those portions of the other family of curves intersected by the lower right corner of the wire give the outside slopes of the mountain-like formations pulled up by the ring.

If the ring is made of wire having a circular cross section and is pulled out, keeping the plane of the ring parallel to the undisturbed surface, the two curves, one from each family, which are at any particular position tangent to it, the meniscus on the inside and the other on the outside, give the shapes of the inner crater and the outer slope of the liquid raised by the ring in that particular position. The last statement involves an approximation. It is assumed that the material of the ring is wetted by the liquid. While it is accordingly to be expected that a film of liquid covers the whole of the ring, this film must be very thin where the ring is not immersed, for the attraction which causes it to adhere extends only a very short distance from the surface. The volume of this film, then, must be small. It is assumed in this discussion that it is negligible in comparison with that held up by the surface tension itself. Those curves that are tangent to the ring are the ones selected because the fact that the ring is wetted implies a zero angle of contact.

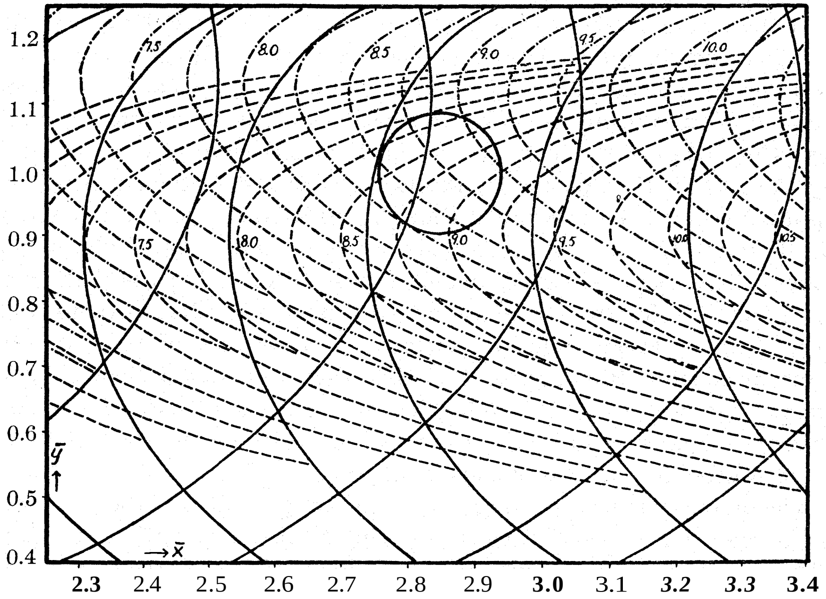
The quantity measured in the experimental procedure of the ring method is the weight necessary to cause the ring to break away from the liquid. This is usually the maximum weight of liquid held up by the ring. It may be calculated from our graphs of Equation **3.** After the capillary constant has been eliminated from the equation, that which corresponds to the volume of the liquid held up by the ring in a particular position will be designated by $\overline{V}$. Its value is found as follows. Integration of Equation **3** gives for the volume below any horizontal section through the outer surface, for example, below the section through the point of tangency of curve and ring

$$\overline{V}_1' = \pi\bar{x}_1^2\bar{y}_1 + \pi u_1\bar{x}_1 \tag{6}$$

and for the volume below any similar horizontal section cutting the meniscus surface

$$\overline{V}_2' = \pi\bar{x}_2^2\bar{y}_2 - \pi u_2\bar{x}_2 \tag{6'}$$

where subscripts 1 and 2 refer, respectively, to the points of tangency of the outer and meniscus surfaces with the ring, and the corresponding $\bar{V}'$ accordingly represents the volume below this section. For the outer curve it is the volume generated by revolving about the axis of symmetry the area bounded by the Z-axis, the y-axis, the line $\bar{y} = \bar{y}_1$ and the curve; for the meniscus it is the volume generated similarly by the area bounded by the y-axis, the line $\bar{y} = \bar{y}_2$ and the curve. This is shown in Fig. **3.** $\bar{V}_1$, the volume outside of the line $\bar{x} = \bar{x}_1$ corrected as discussed below, is obtained by subtracting the volume of the cylinder $\pi\bar{x}_1^2\bar{y}_1$ from $\bar{V}'_1$. From Equation 6 $\bar{V}_1$ is thus seen to be equal to $\pi u_1\bar{x}_1$. From Equation 6' it is seen that $\bar{V}_2$, the volume held up by the ring inside of the line $\bar{x} = \bar{x}_2$ properly corrected, is given by subtracting $\pi\bar{x}_2\bar{y}_2$ from $\bar{V}'_2$, and making the necessary change in sign.



—— Meniscus and disk curves; – – – constant $\pi u_1\bar{x}_1$ (dirk); —·— constant $\pi u_2\bar{x}_2$ (meniscus).

Fig. 2.—Portion of Fig. 1 with constant $\pi u\bar{x}$ lines.

The volume labeled $\bar{V}_3$ in Fig. 2, between the limits $\bar{x} = \bar{x}_2$ and $\bar{x} = \bar{x}_1$, is obtained, allowing for a small correction, by finding the volume generated by revolving the area under *a* curve about an axis. In this case the curve is the cross section of the wire between the points $\bar{x}_2$, $\bar{y}_2$ and $\bar{x}_1$, $\bar{y}_1$ and the axis of revolution is the y-axis. It is accomplished as follows. For convenience the bars above all symbols are dropped in the following derivation. R is the radius of the ring, r is the radius of the wire and h is the height of the bottom of the ring above the x-axis.

$$V_3 = 2\pi \int_{x_2}^{x_1} x\{(h + r) - \sqrt{r^2 - (R - x)^2}\}\mathrm{d}x$$

$$\int_{x_2}^{x_1} x(h + r)\mathrm{d}x = \frac{x^2(h + r)}{2}\Big]_{x2}^{x1}$$

$$\int_{x_2}^{x_1} x\sqrt{r^2 - (R -} \qquad = -\int_{x_2}^{x_1} (R - x)\sqrt{r^2 - (R - x)^2}\,\mathrm{d}x + \int_{x_2}^{x_1} R\sqrt{r^2 - (R - x)^2}\,\mathrm{d}x$$

$$= -\frac{1}{3}\{r^2 - (R - x)^2\}^{3/2}]_{x2}^{x1} - \frac{R}{2}(R - x)\{r^2 - (R - x)^2\}^{1/2}]_{x2}^{x1} - \frac{R}{2}r^2 \sin^{-1}\frac{R - x}{r}\Big]_{x2}^{x1}$$

$$\therefore V_3 = \pi\{(h + r)(x_1^2 - x_2^2) + \frac{2}{3}[(h + r - y_1)^3 - (h + r - y_2)] + R(R - x_1)(h + r - y_1)$$

$$-R(R - x_2)(h + r - y_2) + Rr^2\left(\sin^{-1}\frac{R - x_1}{r} - \sin^{-1}\frac{R - x_2}{r}\right)\} \qquad (7)$$

Of the terms in Equation 7 only the first and last are of appreciable significance in most cases, and just these two were usually used in the calculations. In some cases, however, it was necessary to use the third and fourth.

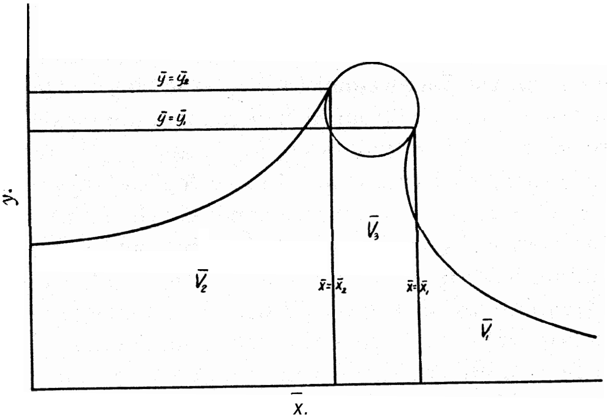


Fig. 3.—Vertical section of liquid raised by ring.

It may seem that another correction should be made for the small volume of the ring which may be inside of the line $\bar{x} = \bar{x}_2$ or outside of that $\bar{x} = \bar{x}_1$. However, this is already allowed for in the calculation of $\bar{V}_3$, when $\sin^{-1}\frac{R - x_1}{r}$ or $\sin^{-1}\frac{R - x_2}{r}$, as the case may be, is greater than $\pi/2$. When these angles are less than $\pi/2$, the lines $\bar{x} = \bar{x}_2$ and $\bar{x} = \bar{x}_1$ cut the surfaces, and the correction is made in the corresponding value of $\pi u \bar{x}$, that is, $\bar{V}_1$ or $\bar{V}_2$. These corrections are, in general, so small as to be negligible in all cases except when R/r is very small.

The total volume held up by the ring in any position is given by

$$\bar{V} = \bar{V}_1 + \bar{V}_2 + \bar{V}_3$$

To facilitate the use of Fig. 1 in these calculations, constant $\pi u\bar{x}$ curves, isochors, for the two families of surfaces have been calculated, and superposed upon Fig. 1. Thus at any point on the map $\bar{V}_1$ and $\bar{V}_2$ may be read off. Unfortunately the necessary interpolations are such as to introduce an error into the conclusions, but this is inherent in the graphical method of solution. Of course, the error may be reduced below any desired limit if enough surfaces are calculated. To attain the precision of the experimental values of Harkins and Jordan more curves than we have provided are needed, although it is estimated that our procedure gives results of the same order of precision as their experimental method. We have been sufficiently precise to convince ourselves of the adequacy of the underlying theory proposed.

A small portion only of the map is reproduced in this paper as Fig. 2. The whole would be quite unintelligible, as well as unusable, because of the reduction necessary for publication, but the portion reproduced serves adequately to demonstrate our procedure. The heavy circle is the cross section of the wire of the ring. In the actual procedure we lay upon the map, which is an enlarged Fig. 1 bearing the constant volume lines, a metal template of this cross section made, of course, to scale, and place its center at a distance from the y-axis equal to $\bar{R}$ for the ring. The points of tangency of the two curves, one from each of the two families of surfaces, with the wire are noted. These points are $\bar{x}_1$, $\bar{y}_1$ and $\bar{x}_2$, $\bar{y}_2$, respectively, and $\bar{V}_1$ and $\bar{V}_2$ are read from the map. $\bar{V}_3$ is calculated approximately from the formula $\pi(\bar{x}_1^2 - \bar{x}_2^2)(\bar{h} + \bar{r})$, thus using merely the first term of Equation 7, which is written as $\bar{V}_{3a}$. $\bar{V}_1 + \bar{V}_2 + \bar{V}_{3a}$ gives an approximate value of the total volume held up. The procedure is repeated, varying $\bar{h}$, that is, moving the template parallel to the y-axis. It is found that as $\bar{h}$ increases, the approximate value of $\bar{V}$ goes through a maximum. This maximum value and a few on either side of it are recalculated more precisely using additional terms of Equation 7. The maximum thus precisely calculated is taken as the maximum volume capable of being held up by the ring, and its weight is what is measured by the ring method.

Harkins and his collaborators plot their values for the corrections to be applied to the usual ring method on a diagram using R^3/V and γ/p as the coordinates, where R is the radius of the ring and $p = W/4\pi R$, a procedure quite analogous to Harkins and Brown's correction curve for the drop weight determination. The corresponding terms in our procedure are $\bar{R}^3/\bar{V}$ and $2\pi\bar{R}/\bar{V}$. $\bar{R}^3/\bar{V}$ is identical with R^3/V because the a^3 in numerator and denominator cancels. $2\pi\bar{R}/\bar{V}$ corresponds to γ/p by virtue of

$$\frac{\gamma}{p} = \frac{4\pi R\gamma}{W} = \frac{4\pi R\gamma}{Vgd} = \frac{4\pi Ra^2}{2V} = \frac{2\pi\bar{R}a^3}{\bar{V}a^3} = \frac{2\pi\bar{R}}{\bar{V}}$$

These quantities have been calculated by the procedure just outlined. The curves given by these variables are found to coincide with the experimental curves within the accuracy of the calculations. Por comparison particular points so calculated are shown in Pig. 4. We are certain that any discrepancies are due entirely to the difficulties inherent in a graphical method and in the fact that enough surfaces have not been calculated; but only those who have made such numerical integrations can appreciate the labor involved in producing even a single curve.

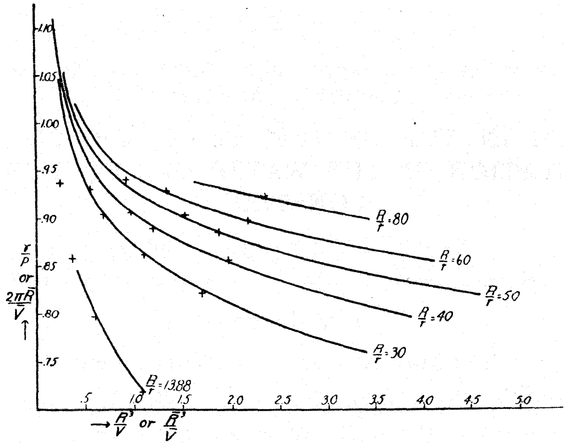


Fig. 4.—Comparison of theory and experiment: ——, experiment (Harkins and Jordan); +, theory (Freud).

The remarkable agreement between the calculated and the experimental values shows that, within the small error of both methods, the same values of the surface tension are obtained, whether the relative corrections of Harkins and his collaborators, or the absolute corrections as calculated by us are used. Thus the ring method, as described by Harkins, Young and Cheng, may now be considered as an absolute method, since by it the surface tension may be determined without reference to any other method.

Conclusions

1. A theory for the ring method of determining surface tension, based on the fundamental Laplace equation describing stable liquid surfaces, has been proposed.

2. This equation has been integrated numerically, thus giving data describing the shapes of the surfaces formed by raising a wetted ring out of a liquid. These data are represented in the paper by a graph of two families of curves. They may be used to supplement the tables of Bashforth and Adams.

3. From these curves it is possible to find certain ratios which are analogous to the dimensions of any particular ring and to the volume of any liquid held up by it. The relationship between three suitable functions of these ratios gives a set of curves which are analogous to those

determined experimentally and which are quite independent of any measurement of surface tension.

4. These curves are found to agree with the analogous experimental curves.

5. The ring method may thus be considered an absolute one for the determination of surface tension.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

EQUILIBRIUM IN THE SYSTEM $Co-CO_2-CoO-CO$. INDIRECT CALCULATION OF THE WATER GAS EQUILIBRIUM CONSTANT

BY P. H. EMMETT AND J. F. SHULTZ

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Introduction

A survey of the literature reveals marked disagreement concerning the value of the equilibrium constant K_1 for the reaction

$$CO + H_2O = CO_2 + H_2 \quad K_1 = (P_{CO_2})(P_{H_2})/(P_{CO})(P_{H_2O}) \qquad (1)$$

Hahn,[1] Haber and Richardt,[2] and finally Neumann and Kohler[3] have obtained directly values for the equilibrium constant. However, Eastman[4] and his collaborators, by measuring the equilibrium in each of the reactions

$$FeO + H_2 = H_2O + Fe \quad K_2 = P_{H_2O}/P_{H_2} \qquad (2)$$
$$FeO + CO = CO_2 + Fe \quad K_3 = P_{CO_2}/P_{CO} \qquad (3)$$
$$SnO_2 + H_2 = Sn + H_2O \quad K_4 = P_{H_2O}/P_{H_2} \qquad (4)$$
$$SnO_2 + CO = Sn + CO_2 \quad K_5 = P_{CO_2}/P_{CO} \qquad (5)$$

and by making use of the relations $K_1 = K_3/K_2 = K_5/K_4$, obtain indirectly a value for the water gas equilibrium constant that differs by about 40% from the directly determined one. The evidence for the validity of the indirect calculation has seemed particularly strong in view of the fact that the results obtained in the $Sn-SnO_2$ system agree so excellently with those in the $Fe-FeO$ system. Accordingly, since we have already determined and published[5] the value of the equilibrium constant for the reaction

$$CoO + H_2 = Co + H_2O \quad K_6 = P_{H_2O}/P_{H_2} \qquad (6)$$

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[1] Hahn, *Z. physik. Chem.*, **44**, 513 (1903); **48**, 735 (1904).

[2] Haber and Richardt, *Z. anorg. Chem.*, **38**, 5 (1904).

[3] Neumann and Kohler, *Z. Elektrochem.*, **34**, 218 (1928).

[4] (a) Eastman and Evans, THIS JOURNAL, **46**, 888 (1924); (b) Eastman and Robinson, *ibid.*, **50**, 1106 (1928).

[5] Emmett and Shultz, *ibid.*, **51**, 3249 (1929).

it seemed of interest to determine experimentally the equilibrium constant for the reaction

$$CoO + CO = Co + CO_2 \quad K_7 = P_{CO_2}/P_{CO} \qquad (7)$$

and thus to obtain an additional set of data from which the water gas equilibrium constant could be calculated.

Experimental

A flow method similar to that described in the previous paper[5] was used in the present experiments. It consisted in passing known carbon dioxide–carbon monoxide mixtures over a large volume of catalyst held at constant temperature and determining the CO_2–CO ratio in the effluent gas. Equilibrium was approached from both the high and low CO_2/CO sides at each temperature; readings were continued until a constant and reproducible value was obtained.

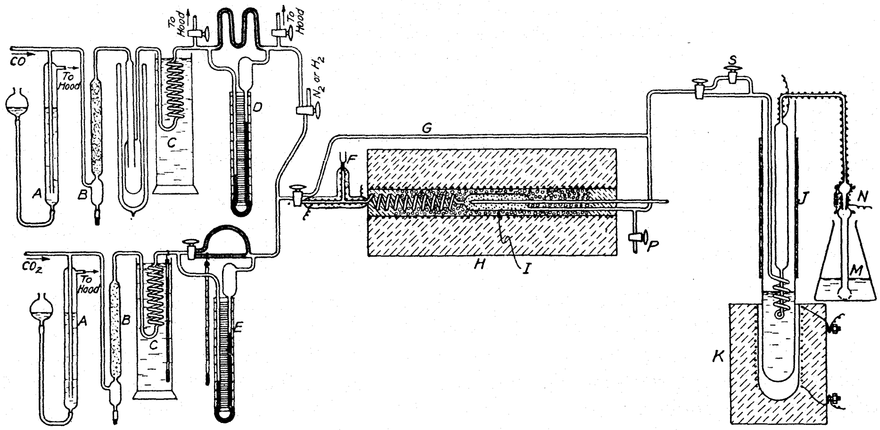

Fig. 1.

The apparatus can best be described with the help of Fig. 1. Commercial carbon dioxide, after being dried by phosphorus pentoxide, was passed through a flowmeter into the catalyst chamber. Carbon monoxide, especially prepared by Thompson in a manner already described,[6] was passed through a liquid-air trap to free it from $Fe(CO)_5$, which experience has shown is likely to accumulate when, as in the present case, the carbon monoxide had been stored for some time in a steel cylinder. The carbon monoxide was then passed through a flowmeter into the catalyst chamber. Necessary overflow bubblers as well as means of conducting to hoods any excess carbon monoxide were also employed as shown. The furnace was the same as that previously used and consisted of a nichrome wound alundum tube packed into a larger iron cylinder with "85% magnesia." The reaction chamber was packed into the center of the alundum tube with mossy copper. A thermocouple well extending along the axis of the glass reaction tube permitted the temperature to be measured throughout the entire length of the Co–CoO mass. The gradient thus obtained did not exceed 3°. The temperature was measured with a calibrated alumel-chromel thermocouple, together with a portable

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[6] Thompson, *Ind. Eng. Chem.*, **21**, 389–390 (1929).

Leeds and Northrup potentiometer indicator. The cold junction correction on the instrument was set correctly several times each day.

In the course of the experiments, streams of pure hydrogen, pure nitrogen and steam were required. Separate stopcocks connected the system to supplies of nitrogen and of hydrogen that had each been purified by passage over hot copper. The steam boiler was sealed off when not needed.

The carbon dioxide flow was measured by means of a carefully calibrated flowmeter. Two methods of calibration were used to avoid any uncertainty as to the rate of carbon dioxide passage. The flowmeter was first calibrated by collecting the carbon dioxide over a saturated sodium chloride solution. Many points were obtained at several flows varying from **10** to **100** cc. of the gas per minute. This calibration curve was checked by a second method that consisted in absorbing the stream of carbon dioxide in a potassium hydroxide weighing bulb and noting the increase in weight per unit time for a given setting of the flowmeter. The agreement obtained in the two calibrations is shown in Table **I**. In actual runs only flowmeter settings were used for which the calibrations in Table **I** were made.

TABLE I

CALIBRATION OF CARBON DIOXIDE FLOWMETER

	Small capillary		Large capillary		
Height of flowmeter liquid, cm.	11.0	27.6	9.0	10.8	18.4
Cc./min., Method 1[a]	10.26	25.75	50.41	60.56	101.29
Cc./min., Method 2[b]	10.33	25.94	50.05	60.17	100.22
Cc./min., average of 1 and 2	10.30	25.85	50.23	60.37	100.76

[a] Carbon dioxide was collected in potassium hydroxide and weighed.

[b] Carbon dioxide was collected over saturated sodium chloride solution and the displaced liquid measured.

The carbon monoxide content of the exit carbon dioxide–carbon monoxide mixture was determined by passage over iodine pentoxide, absorption of the liberated iodine in potassium iodide solution, and titration with **0.001** *N* sodium thiosulfate solution.[7] An approximate entering flow of carbon monoxide was obtained by a flowmeter equipped with a capillary sufficiently small in diameter to permit the passage of only **6** or 7 cc. of carbon monoxide per minute, under a head of **40** cm. of Nujol.

The **0.001** N sodium thiosulfate was standardized by titration against carefully checked **0.00121** *N* potassium permanganate solution. The agreement obtained as shown in Table II between the titrated carbon monoxide and measured carbon monoxide in calibration of the carbon monoxide flowmeter serves as an additional check of the fact that the titrimetric carbon monoxide determination could not be grossly in error. The normality of the thiosulfate was checked daily. The efficiency of the iodine pentoxide toward the oxidation of carbon monoxide was determined at frequent intervals by running blanks on the entering CO_2–CO ratios. In addition, a final check of the efficiency of the iodine pentoxide was obtained at the end of the series of equilibrium measurements by comparing the efficiency of the iodine pentoxide tube held at **100**° with that of two iodine pentoxide tubes in series, the first at **100**° and the second at **140**°. The agreement of the carbon monoxide as determined in these experiments is shown in Table II. It was considered sufficient proof that all carbon monoxide was being quantitatively oxidized to carbon dioxide by the iodine pentoxide in the equilibrium runs.

For the small concentrations of carbon monoxide used in the present experiments it was found entirely satisfactory to maintain the iodine pentoxide at a temperature of

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[7] Vandaveer and Gregg, *Ind. Eng. Chem.*, **Analytical Ed., 1, 129 (1929).**

TABLE II

CALIBRATION DATA

Height of flowmeter liquid, 2.35 cm.; inlet CO,[a] 0.30 cc./min.; time, 5 min.

Cc. $Na_2S_2O_3$	Exit CO Total	Exit CO cc./min.	Cc. $Na_2S_2O_3$	Exit CO Total	Exit CO cc./min.
One I_2O_5 tube at 100°			Two I_2O_5 tubes in series: Tube 1 at 100°; Tube 2 at 140°		
26.03	1.482	0.296	25.76	1.466	0.293
25.70	1.463	.292	25.86	1.471	.294
26.20	1.491	.298	25.85	1.470	.294
26.11	1.485	.297	25.70	1.463	.292

[a] These "inlet CO" flows were taken from an extrapolated calibration curve obtained by measuring volumetrically the carbon monoxide at flows of five and ten cc. per minute. It should be accurate to 5%.

100". Quantitative oxidation of the carbon monoxide with liberation of iodine was thereby obtained without causing any thermal decomposition of the pure iodine pentoxide. Stopcock S was adjusted to produce the same back pressure in the line during the intervals between runs that was produced by the potassium iodide absorption solution during a run. Thus by turning the gas stream through S during the interval between runs a practically constant rate of flow could be produced.

The exit of the iodine pentoxide tube was electrically heated in order to prevent the condensation of iodine. A ground-glass joint was provided in the exit line permitting the portion dipping into the potassium iodide solution to be removed and washed free of any condensed iodine. By such means all traces of iodine evolved in a particular run could be washed into the potassium iodide solution and titrated.

The cobaltous oxide used in the present experiment was the same sample that had been used in a previous determination of the steam–hydrogen equilibrium over cobalt–cobaltous oxide already referred to.[6] It was originally prepared by igniting to 500° some recrystallized cobaltous nitrate containing 0.98% of nickel, reducing this material almost completely with hydrogen, and partially reoxidizing it to cobaltous oxide by a long steaming process at 500°. Its weight as Co_3O_4, at the completion of the ignition in air, was 23 g. Its apparent volume was 30 cc.

At the beginning of the series of runs the cobalt–cobaltous oxide mixture was steamed at 500° until 75% oxidized. Then about 400 cc. of hydrogen was passed through to insure the presence of ample cobalt surface. The hydrogen–steam mixture was removed by flushing with nitrogen. At each of the three temperatures studied, carbon dioxide-carbon monoxide mixtures were passed over the resulting material at such rates of flow as were necessary to obtain equilibrium. From time to time the surface of metallic cobalt was restored by reduction with about 400 cc. of hydrogen. Equilibrium was approached from both sides and readings were taken over a sufficient interval of time to assure the reaching of steady state conditions and to exclude the possibility of temporary surface effects influencing the equilibrium values. In each run readings were taken of the temperature of the air immediately surrounding the capillary of the carbon dioxide flowmeter, temperature of the water-bath through which the carbon dioxide line passed before reaching the capillary, temperature of the reaction tube, time of passage of carbon dioxide, barometric pressure, and back pressure in the reaction system resulting from placing potassium iodide absorption solution on the exit of the iodine pentoxide tube. The volume of carbon monoxide as determined by the thiosulfate titration was also recorded. The CO_2–CO ratio in equilibrium with Co–CoO at each of the three temperatures employed was calculated from these data.

Experimental Results

The values of $K_7 = P_{CO_2}/P_{CO}$ obtained at 450, 515 and 570° are 489.6, 245.9 and 148.4, respectively. Attempts to obtain values at 330° were abandoned because of the sluggishness with which equilibrium was reached at so low a temperature.

In Tables III, IV and V are shown a few typical runs at each of the three temperatures studied. They consist of several groups of consecutive runs taken from a longer series of runs at each of the temperatures. In Col. 2 is

TABLE III

DATA FROM TYPICAL RUNS TEMPERATURE, 450°

	Inlet mixture				CO_2/CO	
Run no.	CO_2, cc./min.	CO, cc./min.	Time, sec.	Exit CO, total cc.	Inlet	Exit
143	25.80	0	600	0.523	∞	492.4
144	25.85	0	600	.521	∞	494.8
145	25.88	0	600	.522	∞	494.8
154	100.86	0.31	300	1.051	325.3	480.3
155	101.22	.31	300	1.057	326.5	479.3
156	100.80	.31	300	1.045	325.1	482.8

TABLE IV

DATA FROM TYPICAL RUNS. TEMPERATURE, 515°

	Inlet mixture				CO_2/CO	
Run no.	CO_2, cc./min.	CO, cc./min.	Time, sec.	Exit CO, total cc.	Inlet	Exit
168	60.03	0.31	300	1 223	193.6	245 7
169	60.03	31	300	1 217	193 6	246.9
170	60 03	.31	300	1 235	193.6	243 3
197	25 55	0	600	1 021	m	249 3
198	25 47	0	600	1.026	m	247 3
201	25 40	0	600	1 033	m	244.9
202	25.40	0	600	'1.037	m	244.0
203	10 10	0	600	0 412	m	244.2
204	10.12	0	600	.415	m	242.8

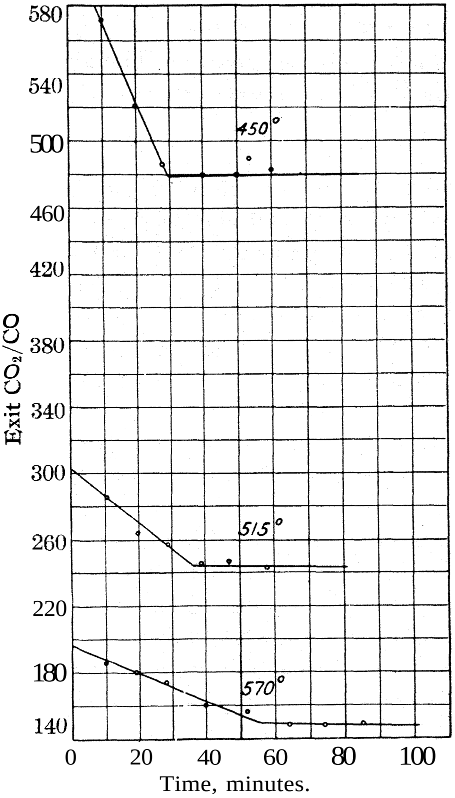
TABLE V

DATA FROM TYPICAL RUNS. TEMPERATURE, 570°

	Inlet mixture				CO_2/CO	
Run no.	CO_2, cc./min.	CO, cc./min.	Time, sec.	Exit CO, total cc.	Inlet	Exit
214	25 58	0	600	1 724	m	147.4
215	25.54	0	600	1 726	m	147 0
216	25.55	0	600	1 716	m	147 9
217	25 57	0	600	1.715	∞	148.1
218	25 59	0	600	1 720	m	147.8
225	102 77	0 99	180	2 077	103 8	148 8
226	102 69	.99	180	2.082	103.7	148 3
227	102 81	.99	180	2 108	103 8	146 7
228	102.56	.90	180	2.053	113.9	150.1
229	102.50	.90	180	2.057	113.8	149 8
230	102.56	.90	180	2.061	113.9	149 5
231	102.39	.90	180	2.059	113.7	149.4

listed the rate of flow of carbon dioxide (S.T. P.) per minute into the reaction vessel. Corrections have been applied as explained later for the temperature of the flowmeter capillary and for the barometric pressure. Column **3** contains the approximate values for the entering flow of carbon monoxide, obtained as described in the footnote to Table II. Column 4 represents the time during which an analytical sample was taken. The total carbon monoxide shown in Col. 5 is that calculated from titration with the sodium thiosulfate. The average of the exit CO_2/CO ratios in Col. 6 of the tables differs slightly from the average of all runs made. This is inevitable, of course, in choosing only a small number of representative runs out of a large number taken.

It was noticed in the course of the work that the first few runs made after a reduction of the oxide surface by hydrogen yielded low values for the CO_2–CO ratio, when pure carbon dioxide was passed over the oxide–metal mixture. Furthermore, the first few runs made after complete oxidation of the surface to cobaltous oxide yielded abnormally high CO_2/CO values, even though the entering CO_2–CO ratio was much less than the normal equilibrium value. Figure 2 gives a few typical curves illustrating this latter effect. In each instance the entering CO_2–CO ratio was 30 to 50% less than the normal equilibrium value. The value of K_7 decreases with time until the normal value results. This is entirely analogous to the effect noted in the determination of the H_2O–H_2 ratio necessary to oxidize cobalt to cobalt oxide.[5]



Pig. 2.—Typical curves Lowing the effect of "surface oxide" on the CO_2–CO equilibrium value. The three series of runs shown were taken immediately after oxidation of the cobalt surface to CoO. The entering CO_2–CO ratios in the 570, 515 and 450" runs shown were 102, 194 and 325, respectively.

The accuracy of the above equilibrium values will depend upon the reliability of the volume of carbon dioxide passing the reaction tube per unit time, the volume of carbon monoxide passing the reaction tube in the same time and the temperature of the reacting cobalt–cobaltous oxide.

Accordingly, each of these determinations will be briefly considered with a view to fixing the maximum and probable errors of the final equilibrium values.

Four possible sources of error in the determination of the carbon dioxide are (1) the uncertainty in corrections for the pressure and temperature variations from the temperature and pressure at which the flowmeter was originally calibrated; (2) the reading error on the flowmeter; (3) the uncertainty in the calibration of the flowmeter; and (4) the uncertainty of the exact temperature of the flowmeter capillary through which the carbon dioxide passed. The first of these sources of error was corrected for by the equation

$$\frac{V_1}{V_2} = \frac{\eta_2 T_2 P_1}{\eta_1 T_1 P_2}$$

where V_1 is the volume of gas (S. T. P.) that passed the flowmeter during calibration when the height of the flowmeter liquid was h_1, the capillary of the flowmeter was at T_1 and the pressure at the exit of the flowmeter P_1; η_1 is viscosity of carbon dioxide at T_1; V_2 is volume of gas (S. T. P.) passing the capillary when the latter is at T_2, the pressure at the flowmeter exit P_2 and the height of the flowmeter liquid again h_1; η_2 is viscosity of carbon dioxide at T_2.

The values for the viscosity of carbon dioxide in the "International Critical Tables" (Vol. V, p. 4) are 147.1 at 23° and 137 at 0°. In making corrections by the above formula, η_2 and η_1 were obtained by extrapolating these viscosity values to the temperature range 25–33°, over which the capillary varied during the series of runs. When, as in the above measurements, T_1 is 29°, P_1 is 750 mm., $(T_1 - T_2) \gtreqless 4°$ in absolute value, and $P_1 - P_2 \gtreqless 10$ mm. in absolute value, it is believed the uncertainties of this correction should be very small, probably ±0.2%. (2) The uncertainty of the flowmeter reading will not exceed 1 mm. This represents an error of ±0.6% at the rates of flow used for most of the runs. (3) From the calibration data of Table I the uncertainty of the carbon dioxide calibration seems to be about ±0.3%. (4) It is assumed that the temperature of the capillary of the flowmeter does not differ by more than ±0.5° from that of the thermometer hanging in air beside it. The summation of the possible errors in the carbon dioxide values thus amounts to *1.3%.

The two sources of error in the carbon monoxide determination are the series of standardization determinations against potassium permanganate and the individual titration in each regular run. The first of these seems not to exceed ±0.3%. Assuming the end-point in the final thiosulfate–iodine titration to be accurate to ±0.2 cc., a maximum error of about ±1.2% would result. Hence the maximum individual error in the carbon monoxide determinations was about ±1.5%.

From a plot of the logarithm of the equilibrium constant against the reciprocal of the absolute temperature, the variation of each constant per degree of temperature variation is readily found to amount to approximately 1% per degree. The temperature was noted at the beginning and end of each run and an average value recorded. The portable potentiometer could be read to ±1°. It is probable, therefore, that errors due to temperature variation did not exceed ±1%. However, in the present maximum error calculation an uncertainty in temperature of ±3° causing a possible error of ±3% in the equilibrium constants for any specified temperature has been assumed.

The summation of the maximum errors that could conceivably be involved in any one reading is thus about 6%. An examination of all the data obtained, however, shows that the maximum deviation from the mean was very much smaller than this calculated possible maximum error. In fact, the maximum deviation of any one reading from the average was 3.9% at 570°, 3.6% at 515° and 2% at 450°. The average deviation was between 1 and 1.3% for the three temperatures. Probable errors calculated by the usual formula on a basis of all of the readings obtained at each temperature (except, of course, those immediately following fresh reduction or oxidation of the catalyst surface) amount to about ±0.3%.

The Equilibrium Constant for the Water Gas Reaction.—The values of K_6 already reported[5] for the temperatures 450, 515 and 570° are 67, 57.5 and 50.3, respectively. From the above K_6 values and the K_7 values determined in the present work, the values of $K_1 = (P_{CO_2})(P_{H_2})/(P_{CO})(P_{H_2O})$ can be readily calculated to be 7.31, 4.31 and 2.94 at 450, 515 and 570°, respectively. Most workers have expressed their results in terms of $K_{wg} = 1/K_1$. The present calculated values of K_{wg} are accordingly the reciprocals of the above and equal to 0.137, 0.232 and 0.340 at the above temperatures. These values agree closely with 0.140, 0.232 and 0.345 obtained in the direct measurements of Neuman and Kohler. In Fig. 3 are plotted values for log K_{wg} against $1/T$. The results of the direct determination of K_{wg} by Hahn,[1] by Haber and Richardt[2] and by Neumann and Kohler[3] are included for comparison. The indirectly determined values of Eastman and Evans[4] are also indicated.

A consideration of the maximum errors that could reasonably be included in the equilibrium values both in the system Co–H_2O–CoO–H_2 and the system Co–CO_2–CoO–CO indicates that the excellent agreement between the values of the water gas constant indirectly determined with the help of Co–CoO mixtures and the directly determined values is truly significant and not a coincidence resulting from experimental error. Assuming a temperature reading accurate to ±3°, and an error of ±0.5% in reading the hydrogen, the values given in the previous paper for the H_2O–H_2 ratio in equilibrium with cobalt–cobaltous oxide are accurate to

±1.5%. Accordingly, the summation of all the maximum errors for the two sets of experiments could not, it seems, exceed 7.5%. The probable errors, as calculated from all readings taken in both systems, total ±0.5%. The conclusion seems warranted that the cobalt–cobaltous oxide system affords a reliable indirect means of obtaining values for the water gas constant. The reaction both with steam–hydrogen and with carbon dioxide–carbon monoxide is remarkably free from complications. No oxides other than cobaltous oxide are present, as was established by x-ray powder photographs of the samples used. Tests for carbon or carbide in the cobalt after the carbon dioxide–carbon monoxide equilibrium were practically negative, 0.06% carbon only being found in each of two samples analyzed.

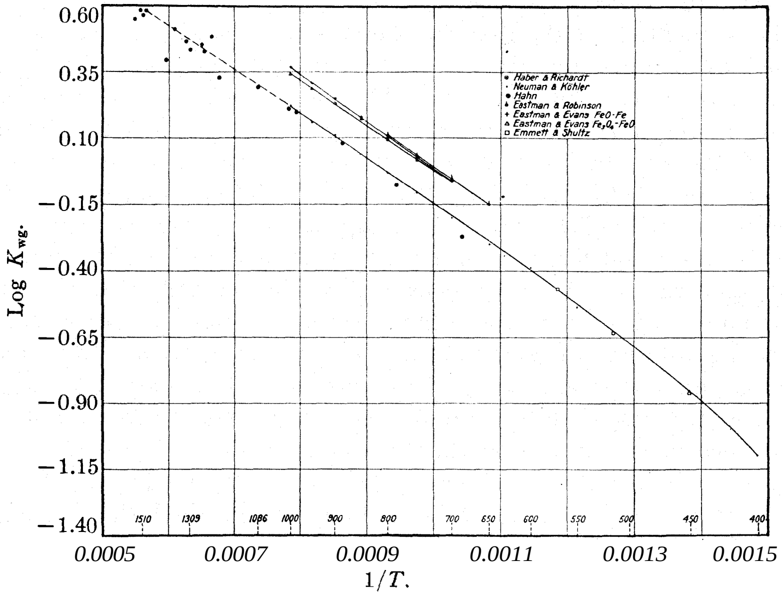


Fig. 3.—Variation with $1/T$ of $\log K_{wg}$ where $K_{wg} = (CO)(H_2O)/(CO_2)(H_2)$. The values of Haber and Richardt, Neumann and Kohler and Hahn are all directly measured values; those of the other authors are the indirect, calculated ones.

In view of the fact that the indirectly determined values of K_{wg} obtained from equilibria of Reactions 6 and 7 were calculated from experimental data obtained over the temperature range 450 to 570°, one cannot, strictly speaking, compare the values so obtained with those obtained by indirect means at higher temperatures. Since it does not seem reasonable, however, to expect sudden changes with temperature in the values of the equilibrium constants of Reactions 6 and 7, between 570 and 700°, one can conclude that the present indirectly determined values of K_{wg} not only verify the directly determined water gas values of Neumann and

Kohler below 570°, but also add a very considerable weight to their direct determinations at higher temperatures.

It is not the purpose of the present paper completely to review all of the other indirect determinations of the water gas equilibrium constant or to attempt therein to explain the discrepancies that now seem to exist. Nevertheless, a few observations will perhaps be worth while.

The experimental work of Eastman and Robinson[4b] upon the determinations of the equilibria of Reactions 4 and 5 in the $Sn-SnO_2$ system seems to have been carefully and accurately done. We are unable to suggest at present any plausible reason why the resulting indirectly calculated water gas constant should be in error. The fact that one of the phases involved in the two equilibria was a liquid and might possibly have been appreciably different in composition in Reaction 5 than in Reaction 4, due to possible dissolved tin carbide, or oxide, offers a slight but entirely unconfirmed source of difficulty.

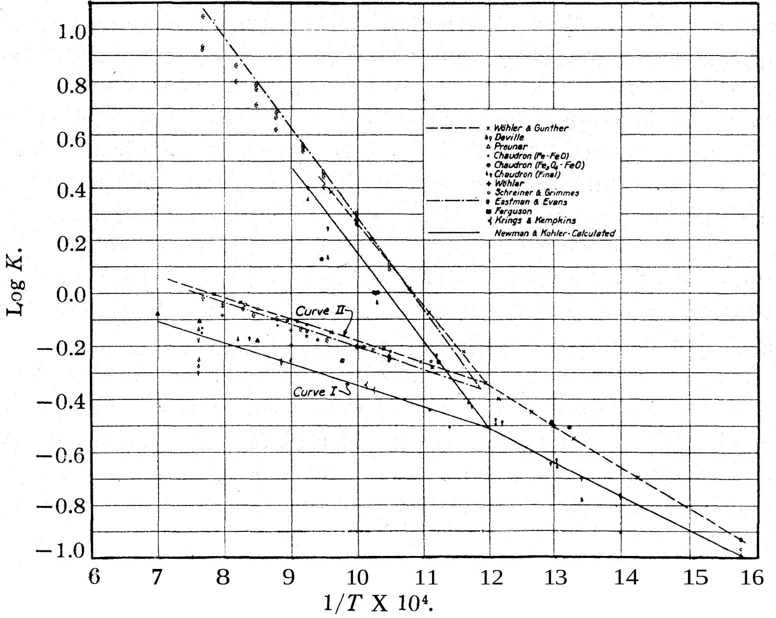


Fig. 4.—Variation with I/T of log K, where $K = (H_2O)/(H_2)$ in equilibrium with $FeO-Fe$, $FeO-Fe_3O_4$ or $Fe-Fe_3O_4$. Curve I is calculated by combination of equilibrium constants for the Fe–C–O system and the direct water gas constants of Neumann and Kbhler. Curve II is the experimental curve of Wohler and Giinther.

It has seemed to us, however, that indirect calculaton of the water gas constants involving the equilibrium constant for Reaction 2 are more open to question. In Pig. 4 are plotted the principal determinations that have been made of the ratio of steam to hydrogen in equilibrium with Fe–FeO at various temperatures. Curve I has been calculated by combining the generally recognized best values for Reaction 3 as chosen by Eastman[8] with the directly determined water gas equilibrium constants of Neumann and Kohler. Any experimental points for the steam–hydrogen equilibria of Reaction 2 will, assuming always the correctness of the Fe–C–O diagram of Eastman, give indirectly calculated values of the water gas constant in perfect agreement with the direct. It can be seen at a glance that the experimental values for the most part fall into two groups. Those of Chaudron,[9] of Deville,[10] of Preuner,[11] of Ferguson[12] and of Krings and Kempkens[13] all agree fairly well with Curve I. The values of the other workers[14,4a] shown in the diagram agree much more closely with Curve II drawn by Wohler and Günther[15] as a representative locus of their own experimental points. We believe it is especially significant that the recent experimental values for the equilibrium constant reported by Krings and Kempkens were obtained by a flow system and are in good agreement with Curve I. Work is now being carried on in this Laboratory to test a possible source of difficulty that has thus separated the experimental observations to date into the two groups. Further discussion of these results will accordingly be deferred to a later paper.

It seems, then, that a correct and fair statement concerning the value of the water gas equilibrium constant must admit of the following.

1. The direct determinations by Neumann and Kohler are in fair agreement with those of Hahn, and of Haber and Richardt. They seem to have been carefully done and are not open to any apparent sources of gross error.

2. The present indirect calculation of the water gas constant from the equilibria for the systems Co–H_2O–CoO–H_2 and Co–CO_2–CoO–CO at temperatures of 450 to 570° agrees well with the directly determined values of Neumann and Kohler. The solid phases seem free of solid solution effects and carbide formation. It is believed the agreement is real and significant.

3. The indirect calculation by Eastman and Robinson involving the Sn–SnO_2 equilibria of Reactions 4 and 6 give values about 40% higher than the directly determined values. No probable cause of the discrepancy is as yet apparent.

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[8] Eastman, THIS JOURNAL, 44,975 (1922).

[9] Chaudron, *Compt. rend.*, 159,237 (1914); *Ann. chim. phys.*, 16,221 (1921).

[10] Deville, *Compt. rend.*, 70, 1105, 121 (1870); 71, 30 (1871).

[11] Preuner, *Z. physik. Chem.*, 47,385 (1904).

[12] Ferguson, *J. Washington Acad. Sci.*, 13,275 (1923).

[13] Krings and Kempkens, *Z. anorg. allgem. Chem.*, 183,225 (1929).

[14] Wohler and Balz, *Z. Elektrochem.*, 27, 406 (1921); Schreiner and Grimes, *Z. anorg. Chem.*, 110, 311 (1920).

[15] Wohler and Günther, *Z. Elektrochem.*, 29,276 (1923).

4. The indirect calculations involving the Fe–H_2O–H_2 equilibria fall principally into two groups, the one agreeing fairly well with the directly measured values, the other being some 40% higher.

Summary

The value of the equilibrium constant $K_7 = CO_2/CO$ for the reaction $CoO + CO = Co + CO_2$ has been determined by a flow system at 450, 515 and 570°, to be 489.6, 245.9 and 148.4, respectively. Combination of these values with the previously determined constant $K_6 = H_2O/H_2$ for the reaction $CoO + H_2 = Co + H_2O$ gives indirect values for the water gas constant $K_{wg} = (CO)(H_2O)/(CO_2)(H_2)$ that are in good agreement with the values determined directly by Neumann and Kohler. The present status of the disagreement between some of the indirectly determined values for K_{wg} and the direct values of Neumann and Kohler is summarized.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

A SCREENED BRIDGE FOR THE MEASUREMENT OF ELECTROLYTIC CONDUCTANCE. I. THEORY OF CAPACITY ERRORS. II. DESCRIPTION OF THE BRIDGE

BY THEODORE SHEDLOVSKY

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Introduction

Kohlrausch's classical method for measuring the electrical conductance of solutions has had the benefit of numerous improvements by many workers. The researches of Washburn[1] were particularly valuable in stimulating accurate conductance work in this country. Morgan and Lammert[2] have discussed some of the sources of error in the electrical arrangement used in the method, with valuable references to previous work. Of particular importance from the standpoint of precision measurements has been the comparatively recent introduction of vacuum tube alternating current generators and amplifiers for providing currents of symmetrical wave form, on the one hand, and increasing the sensitivity of the detector on the other.[3] Jones and Josephs[4] have described in a very detailed paper a direct reading alternating current bridge embodying these new features.

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[1] Washburn and Bell, THIS JOURNAL, 35, 177 (1913); Washburn, *ibid.*, 38, 2431 (1916); Washburn and Parker, *ibid.*, 39, 235 (1917).

[2] Morgan and Lammert, *ibid.*, 48, 1220 (1926).

[3] Hall and Adams, *ibid.*, 41, 1523 (1919); Jones and Bollinger, *ibid.*, 51, 2407 (1929).

[4] Jones and Josephs, *ibid.*, 50, 1049 (1928).

Their paper also includes a valuable and comprehensive study of various sources of error from the electrical standpoint in the Kohlrausch method as it has been generally used.

Important features of Jones and Josephs' bridge are the abandoning of the circular slide wire (which is capable of introducing a disturbing unsymmetrical inductance in the measuring circuit) and the use of a suitable earthing device for the bridge for minimizing disturbing earth capacity effects. They have, however, condemned the use of electrostatic screening of the bridge.[5] The use of screening, when properly designed, for the entire bridge has decided advantages. Since the readings are unaffected by the movements of the observer, a screened bridge is more convenient to operate than an unscreened one. Without adequate shielding, delicate balances are difficult to make due to shifting capacities introduced by the hands of the observer, etc. Also, with suitable screening, measurements of high precision are possible under conditions existing in modern laboratories in which other electrical work is certain to be in progress. Under such conditions the use of an unshielded bridge is at times troublesome if not impossible.

In Part I of this paper the theory of disturbing capacity effects in an alternating current Wheatstone bridge circuit is discussed, with reference to the underlying principle of the apparatus as a measuring instrument. Also, the basis for designing proper screening is developed.

In Part II, a shielded alternating current bridge for measuring electrolytic conductance with a high degree of precision is described. The main problem in the design of such a bridge is the fixing and the proper balancing of "stray couplings" in the apparatus.

PART I. THE THEORY OF EARTH CAPACITY ERRORS IN THE A. C. WHEATSTONE BRIDGE

1. **Stray** Couplings.—When a direct current flows through a conductor, leakage can take place only through inadequate insulation. With alternating currents, the case is more complicated because the current may also leak away through electrostatic and electromagnetic linkings, commonly known as "stray couplings" with the surroundings. Such stray couplings may be electrostatic capacities between the parts of the cirduit and capacities between these parts and the ground. There may also be mutual inductive effects due to linkages with stray magnetic fields. The effects produced by these couplings vary with the frequency, being more troublesome at higher frequencies.

Stray electromagnetic couplings are particularly important in the case

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[5] Their conclusions are based on tests made with a screen placed near one branch of the bridge network, which introduced an *unbalanced* earth capacity effect into the circuit. Such a test does not prove, however, that electrostatic screening cannot be used without error if it is properly designed.

of parts of circuits, such as transformer coils, which have appreciable inductance. These mutual inductive couplings may be reduced by using materials of high permeability in the cores of the transformers, by shielding stray fields with screens of high permeability, or by sufficiently separating the branches of the circuit having high inductances from each other. In the case of a Wheatstone bridge for measuring electrolytic conductance, the only branches in the network capable of very serious inductive coupling with each other are the detector and the oscillator. The best plan is to avoid the necessity of electromagnetic screening, which is always difficult and seldom completely satisfactory. This is readily accomplished by removing the oscillator to a sufficient distance from the detector, which is more conveniently located near the bridge, and avoiding as much as possible the introduction of stray inductance in the bridge itself. A distance of 10 to 15 feet between the detector and the oscillator is usually sufficient.

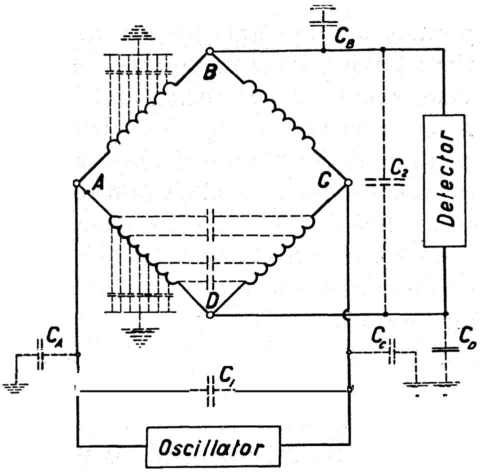

Fig. 1.

Electrostatic couplings existing between various branches of a circuit, directly or to ground, cannot be eliminated entirely in this simple manner without introducing another difficulty. The difficulty is that excessive separation of all the branches of the bridge from each other and from ground, besides being inconvenient, introduces additional inductance into the network because of the increased length of leads required. The result of this increased looping is that although capacitative couplings are reduced, inductances capable of disturbing the bridge balance are thus added, since the bridge balance may be changed by the inductive effect of varying stray fields enclosed.

In Fig. 1 is shown a diagram of a bridge supplied with alternating current, indicating the position of some of the capacitative couplings. The capacity paths from one lead of the oscillator to the other, either directly (C_1) or through ground (C, and C_c in series), merely shunt the current input, and do not affect the bridge balance. Similarly, the coupling between the leads to the detector does not influence the bridge reading, merely shunting the detector. However, couplings are possible which may disturb the balance of the bridge. For example, current leaking from the branch AD, through CB to the terminal B, and back to the oscillator through the branch BC, would have an effect on the bridge balance. (It should be pointed out that the bridge terminals A, B, C and D include the leads appended to them since if they are not too long their resistance is usually negligible.) Although some of these numerous possible paths will tend to neutralize each other, the effects of these paths must be controlled; otherwise, the bridge readings will depend on the relative positions of the units in the circuit and on the surroundings.

Precise measurements are not possible unless these troublesome couplings are neutralized by being made symmetrical with respect to the terminals of the detector. It is not possible to avoid electrical asymmetry entirely in the construction of the apparatus, particularly if the bridge is used for measurements with various frequencies of current, requiring readjustments in the oscillator, or perhaps different oscillators. Neither is it practicable to reduce these couplings so as to make them negligible, especially at the higher frequencies, and in the measurement of dilute solutions having large resistances. For these reasons it is necessary to provide means for controlling and balancing these disturbing effects. This is accomplished (a) by properly designed shielding[6] and (b) by the "Wagner earthing device," both of which will be discussed below. Shielding makes it possible to fix definitely and to control the possible interbranch capacities. Before discussing the effect of capacity couplings on the bridge as a whole, it is first necessary to consider the effect on the impedance of *a* single branch due to the capacity between it and the ground (or a surrounding screen).

2. Effect of Earth Capacity on a Conductor.—In general, with a conductor carrying alternating current, there will be present a distributed capacity of total magnitude c to earth, or to a surrounding screen, as indicated in Fig. 2a, where OR is the conductor of impedance[7] R, and S is the ground or screen. In Fig. 2b is shown a special condition which will help in the consideration of a more general case. In this special case the total capacity from OR to S is concentrated at some point P, between O and R. Let [x] be the impedance from O to P, [y] the impedance from P to R and [z] the impedance from P to S. Let us now substitute for the

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[6] The necessity of electrostatic screening for measurements at frequencies of, say, above 10,000 cycles is generally recognized. See for example G. A. Campbell, "The Shielded Balance," *Electrical World,* April, 647 *(1904);* W. S. Shackelton, "A Shielded Bridge for Inductive Impedance Measurements," *Bell System Technical Journal, 6,* 142 (1927); J. G. Ferguson, "Shielding in High Frequency Measurements," *ibid.,* 8, 560 (1929).

[7] Ohm's law can be applied to sinusoidal alternating currents if vector symbols instead of scalar symbols are used. On this basis the impedance operator, which is analogous to resistance in D. C., is defined as the vector voltage divided by the vector current. See B. Hague, "A. C. Bridge Methods," pp. 32–35; R. M. Wilmotte, *Phil. Mag.,* 6, 788 (1928).

arrangement connecting the points O, R and S as in Fig. 2b, the arrangement shown in Fig. 2c. which we shall prove can be made equivalent by the "Kennelly $\tau - \pi$ transformation."[8] In Fig. 2c $[\alpha]$,$[\beta]$ and $[\gamma]$ are the impedances connecting the three terminals of interest, O, R and S. By equivalence of the two circuits (shown in Figs. 2b and 2c) is meant that the potentials of O, R and S are the same at any instant in both arrangements. Thus, for example, the impedante operators x + y must be equal to α and $\beta + \gamma$ in parallel. (The letters in brackets [x], $[\alpha]$, etc., refer to impedances; x, α, etc., refer to the corresponding impedance operators.) We consequently get the following relations

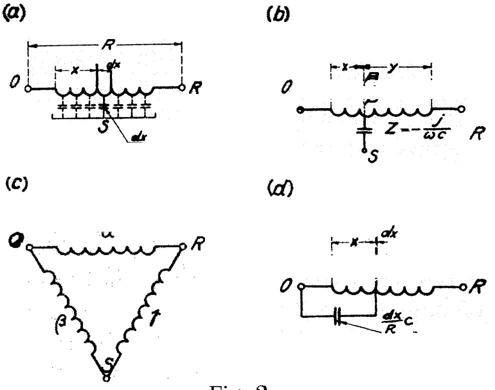

Fig. 2.

$$\frac{1}{x+y} = \frac{1}{\alpha} + \frac{1}{\beta+\gamma} \tag{1}$$

$$\frac{1}{x+z} = \frac{1}{\beta} + \frac{1}{\alpha+\gamma} \tag{2}$$

$$\frac{1}{y+z} = \frac{1}{\gamma} + \frac{1}{\alpha+\beta} \tag{3}$$

Solving, we obtain the equations

$$\alpha = x + y + \frac{xy}{z} \tag{4}$$

$$\beta = x + z + \frac{xz}{y} \tag{5}$$

$$\gamma = y + z + \frac{yz}{x} \tag{6}$$

(a) Capacity Concentrated at the Midpoint.—Now, referring again to Fig. 2b, if we consider R a resistance with its total capacity to the ground (S) concentrated at the midpoint, $x = y = R/2$; $z = -j/\omega c$, where c is the total capacity to ground. $\omega/2\pi$ is the frequency and j is the "reactance" operator.[9] Substituting these values in (4), (5) and (6) we obtain

$$\alpha = R + j\,\frac{R^2wc}{4} \tag{7}$$

$$\beta = \gamma = \frac{R}{2} - j\left(\frac{1}{\omega c/2}\right) \tag{8}$$

---

[8] This transformation has been used by Butterworth [*Proc. Phys. Soc.*, **33**, 312 (1921); *ibid.*, **34**, 8 (1922)] and more recently by Bartlett [*J. Sci. Instruments*, **6**, 277 (1929)] in dealing with the effects of earth capacities.

[9] $(j)^2 = -1$. The reactance due to a capacity c is $-(j/\omega c)$; the reactance due to an inductance L is $j\omega L$. See, for example, B. Hague, "Alternating Current Bridge Methods," p. 35.

That is, due to earth capacity effects, the resistance R between the points O and R is modified by a reactance $R^2\omega c/4$ (this may be considered to be an inductance of magnitude $R^2c/4$ in series with the resistance R) and by the impedances (8) from O and R to ground (S) (these may be considered to be capacities of magnitude $c/2$ in series with a resistance $R/2$).

(b) Capacity Uniformly Distributed.—The more general case of a distributed capacity, as shown in Fig. 2a, is somewhat more complicated to deal with rigorously. However, the values of α, β and γ for this case are approximately represented by Equations 7 and 8. This assumes, of course, the approximation that the total distributed capacity is represented by a single capacity from the middle of the arm to the screen. If the capacity is uniformly distributed, the effect on α due to the differential capacities $(dx/R)(c)$ from the differential proportions dx/R (see Fig. 2) is obtained from Equation 4 to a first approximation by integration as follows[10]

$$d\alpha = x + R - x + j \,\text{''}\frac{(R - x)\omega c dx}{R} \tag{9}$$

$$\alpha = R + \int_0^R \frac{x(R - x)\omega c dx}{R} = R + j\frac{\omega R^2 c}{6} \tag{10}$$

Equation 10 shows that the resistance of OR, due to the distributed earth capacity effect, behaves as a resistance R in series with an inductance $R^2c/6$.

(c) Impedance Directly Connected to Earth or Screen.—Another case of interest is one in which the ground or screen S is connected to one terminal of the impedance (Fig. 2d), since screens are often so connected, and bridges are frequently grounded directly from one terminal. The effect due to the capacity from a differential section to the screen S (or earth) is a shunting impedance [dz]. As before, $-j(R/\omega c dx) = dz$.

The total impedance operator, then, from O to R is

$$Z_{(OR)} = \frac{1}{\frac{1}{x} + j\frac{\omega c dx}{R}} + R - x = x - j\,\omega c x^2 dx + R - X = R - j\frac{\omega c x^2 dx}{R} \tag{11}$$

neglecting terms of higher order.[11] Integrating from $x = O$ to $x = R$

$$Z_{OR} = R - j\frac{\omega c r^2}{3} \tag{12}$$

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[10] For a more rigorous treatment of this uniformly distributed case, see **A. E.** Kennelly, "Electric Lines and Nets," McGraw-Hill Book Co , New York, pp. 61, 395. The method of integration (Equations 9 and 10) used below for obtaining α in this distributed case amounts to neglecting higher order terms in the rigorous treatment which involves the use of hyperbolic functions. However, no such approximations are involved in obtaining Equations 7 and 8.

[11] This derivation involves the approximation that the differential capacity effects act independently. For a more rigorous derivation see R. Davis, **J** *Sci. Instruments*, *5*, 306 (1928).

In this case we see that the earth capacity effect introduces a negative inductance in series with it of magnitude $\boldsymbol{R^2c/3}$.

3. Earth Capacity Effect on the **Bridge** Circuit.—In the light of the discussion in the previous section we may now view the effect of "stray couplings" on the bridge network. We shall assume that direct couplings between the branches have been avoided by shielding. Assuming, then, that the branches of the bridge are so shielded from each other by screens, and making the Kennelly $\tau - \pi$ transformation for every branch, the bridge with its capacity couplings to ground can be represented as in Fig. **3.** The segments L_1, L_2, etc., represent the inductive effects discussed above produced in the branches by the earth capacities. AE, BE, CE and DE are the impedances from the four bridge terminals to ground at E. Each of these impedances includes the separate earth capacity effects from the three branches (corresponding to the various β and γ terms, Equation 8) meeting at each terminal of the bridge network. In addition, there are the capacities to earth from the terminals (and leads) A, B, C and D. For instance, (1) is a resistance in series with a capacity due to AB; (2) is a similar, though not necessarily equal, impedance due to AD; **(3)** is another one due to the oscillator branch; and (4) is a capacity from A to E, due largely to the lead from the oscillator. All these in parallel constitute AE.

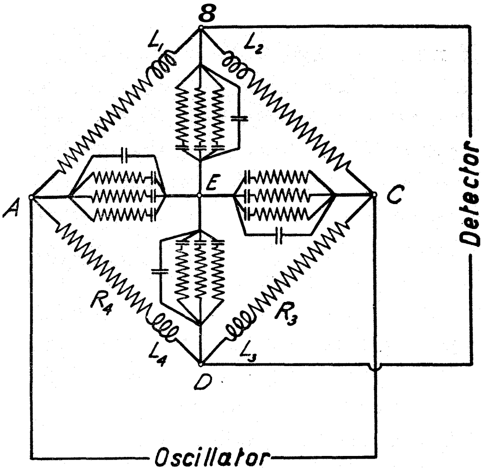

Fig. 3.

It should be noted that the representation of the bridge in Fig. **3** takes into account the distributed dissipations of current from the branches in the circuit to the screens and earth. The advantages of the artifice used in this representation are that it shows the effects produced on the branch impedances from the standpoint of the four terminals of the bridge, making clear the necessary conditions for proper bridge balance, and shows the limitations which must be observed in designing suitable screening so as not to introduce errors in the measurements.

When the bridge is balanced, the terminals B and D are at the same potential, both in magnitude and in phase. That is, the potentials are equal at every instant and no current flows between the two points through the detector. Referring to Fig. **3,** if V is the potential between two points at balance

$$V_{AB} = V_{AD} \text{ and } V_{BC} = V_{DC} \tag{a}$$

This gives by the Vector Ohm's Law[12]

$$\frac{I_{AB}Z_{AB}}{I_{BC}Z_{BC}} = \frac{I_{AD}Z_{AD}}{I_{DH}Z_{DC}} \tag{b}$$

where I is the current and Z the impedance. Now, if the points B and D are brought to the same potential as the ground E, there will be no current flowing in either BE or DE, and the conditions

$$I_{AB} = I_{BC} \text{ and } I_{AD} = I_{DC} \tag{c}$$

will be fulfilled. (There are only three possible paths for current from B or D, when no current flows in the detector.)

Then

$$\frac{Z_{AB}}{Z_{BC}} = \frac{Z_{AD}}{Z_{DC}} \tag{d}$$

If no errors are to be introduced into the measurements, the ratio arms (AD and CD) should be identical in all respects in the case of a direct reading (equal ratio) bridge ($Z_{AD} = Z_{DC}$). Not only must the resistances R_4 and R_3 be equal, but the inductances L_4 and L_3 must also be equal. The latter need not, however, necessarily be negligible, since it is quite feasible to have two equal coils, of similar construction, similarly screened so that, practically, $R_4 = R_3$ and $L_4 = L_3$, in which case $Z_{AD} = Z_{DC}$. Nevertheless, slight differences, in resistance particularly, are likely to occur. This, as well as slight unbalances in the I, terms due to screen capacity, are automatically corrected for if two readings are taken, one with the ratio arms reversed. The average value (strictly speaking, the geometric mean) gives the correct measurement.

However, the characteristics of the measuring branch and of the unknown (cell) cannot be considered identical as in the case of the ratio arms. That is, it is not possible to shield the two with relatively close screens, and feel assured that the capacity effects are similar in both cases. However, shielding is desirable from the standpoint of screening out external influences which may affect the circuit. The correct procedure, therefore, is to shield these branches not closely, but at a sufficient distance to make the effect of the capacity on the impedance negligible under the limiting conditions existing in measurements. If the upper frequency range does not exceed 4000 cycles, direct test showed that a separation of 2.5 inches between the coils of the resistance box (or cell) and the shield introduces a negligible error. That is, the terms L_1 and L_2 in Fig. 3 are negligible.

If these conditions for the ratio arms and the other two branches in the bridge are fulfilled (L_1 and L_2 negligible, $L_3 = L_4$, $R_4 = R_3$, no current in BE or DE) then Equation d reduces to

$$Z'_{AB} = Z'_{BC} \tag{e}$$

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[12] See Hague, Ref. 9, p. 32.

(2' is the impedance free from earth or screen effect)[13] which is the correct balance condition for an equal ratio bridge without error. Jones and Josephs[4] state in their paper that the necessary condition for the validity of Equation e is that no current whatever escape from any of the bridge parts. Of course, if that is so, correct balance is obtained at once. Practically this is not possible. However, as shown above, correct balance, without error in the measurements, is quite attainable when the proper precautions are observed in spite of a certain amount of current leakage from at least some of the branches.

4. The Wagner Earthing Device.—One of the conditions for the validity of Equation e is that the terminals B, D and E (Fig. 3) be at the same potential. This may be done by adjusting the earth impedances AE and CE until no current flows in the detector connected from E to B (or D), when the main bridge (ABCD) is also balanced. That is, $Z_{AE}/Z_{CE} = Z_{AB}/Z_{CB} = Z_{AD}/Z_{CD}$. This is the principle of the device. Since Z_{AE} and Z_{CE} are mixed impedances, consisting of resistance and capacity, the adjusting impedance must similarly comprise a variable resistance and reactance. The reactance may be either a capacity or an inductance, or both, since any impedance may be balanced by such combinations. It is merely necessary to adjust the impedances Z_{AE} and Z_{CE} to the proper ratio.

The scheme used by Jones and Josephs,[4] who, however, do not discuss the theoretical basis of the device, is a very convenient one. It consists of shunting AE and CE with resistances permitting of sufficient variation in adjustment, and a variable condenser from A to E, or C to E, as required. The advantage of their method lies principally in the fact that for the same delicacy of adjustment condensers of lower capacity can be used than would be required with series resistance and capacity combinations.[14]

An examination of Fig. 3 shows the limitations of connecting the ground point E directly to B or D, and securing balance by the adjustment of a condenser in parallel with the necessary branch. Evidently, except in the case of accidental balancing between AE and CE, the bridge reading will not be free from error. The magnitude of the error will depend on the magnitudes of AE and CE and on the extent of their unbalance. It is, however, possible to determine the unbalance between AE and CE, and then to calculate the error thus introduced in the measurements.

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[13] This impedance may be a pure resistance. The somewhat more complicated case of a cell for measuring electrolytic conductance will be discussed in a later paper. However, if the cell impedance is of sufficiently low-phase angle, it can be regarded as a resistance.

[14] Jones and Josephs deserve the credit for describing the proper use of the earthing device for balancing the earth admittances in *a* conductance bridge for work with solutions, although the underlying principle of the method is due to Wagner.

This scheme, though feasible in certain types of impedance measurements, is inconvenient since it requires an estimation of the earth capacity with subsequent calculations. For a bridge designed to measure electrolytic conductance the Wagner device is simpler and preferable.

PART II. A SCREENED ALTERNATING CURRENT WHEATSTONE BRIDGE

The shielded bridge, which was discussed from the theoretical standpoint in Part I, is shown diagrammatically in Fig. 4. The detector and oscillator are connected to the bridge by duplex cables inclosed in flexible copper shielding which is grounded. The oscillator and the earthing circuit W_R, W_C are connected directly to terminals of the measuring branch and of the conductivity cell, at M and N.

1. Balancing Condensers.—A twin (double) variable air condenser K is connected across the measuring resistance (MS) and the cell (BN) as shown, for balancing out the reactance of the cell, due to polarization at the electrodes. The ordinary type of single variable condenser has a disadvantage. It is sometimes impossible to get complete balance in the bridge with it, owing to the fact that the residual zero capacity is too large for the required setting. The twin type, which makes it possible to remove. capacity from one side, adding it to the other, avoids this difficulty, and does not require a switch for shifting the condenser from one branch to the other. The entire condenser K consists of two such twin condensers. One is of 250$\mu\mu$f. capacity, easily reconstructed from the "tandem type" condenser made by the General Radio Co. The other, connected in parallel witli the first, is similarly constructed from two micro condensers. The latter has a maximum capacity of about 10$\mu\mu$f. and it is provided with a "Vernier" control knob, allowing of very delicate adjustment.

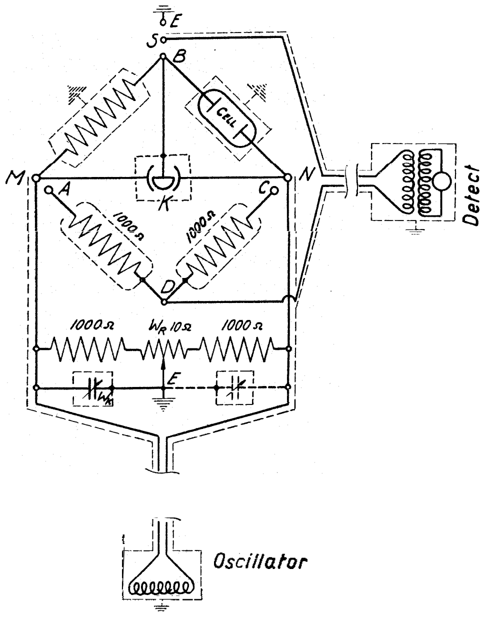

Fig. 4.

2. Ratio Arms.—The ratio arms are connected to the bridge by means of a double pole double throw reversal switch (not shown in Fig. 4). In making determinations the mean of readings with the ratio arms in the two reversed positions is taken. This procedure corrects for slight variations in the resistances (and reactances) of the ratio coils, and avoids the necessity of adjusting them to perfect equality. The ratio coils are surrounded by local symmetrical shields connected to the junction point D. The shield localizes the total distributed capacity of the ratio arms at point D, and avoids the possibility of any stray couplings directly with these important branches of the bridge.

The ratio arms consist of two closely matched Ayrton–Perry coils of 1000 ohms resistance which are wound on flat bakelite cards. It has been shown in Part I that the effect of the distributed capacity in these coils will add an inductance of magnitude $-cR^2/3$ to them. For this reason it is important to make shielding the same around the two ratio arms. In our arrangement the flat coils are mounted parallel to each other, symmetrically between three parallel copper plates spaced 1.5 inches apart. The plates are soldered to a copper strip joining the two resistance coils.

3. The Detector.—The detector consists of a two-stage audio transformer coupled amplifier with sensitive telephones. The output from the bridge is fed into the primary winding of the first transformer. By means of the switch S in Fig. 4, the detector may be connected across DB, for recording the balance in the main bridge, or across DE, for the earthing adjustment.

4. The Earthing Circuit.—The earthing circuit consists; of two 1000-ohm bifilar coils (Leeds and Northrup) and a 10-ohm rheostat (W_R) connected as shown in Fig. 4 to the ratio arm extremities, and to ground. In addition, there is a variable air condenser, with a "Vernier" control knob connected between the earth E and the point A (or C, as required).

Various parts of the bridge, including the oscillator and detector, are shielded from external electrostatic disturbances by the earthed metal shields surrounding them. The various earth points E are all brought together by soldered connections.

The ratio arms, earthing resistances, condensers K, and the reversal and detector switches ("Federal Anti-capacity Switches") are mounted in a grounded copper screened box, as shown diagrammatically in Fig. 5. The top of the box consists of a brass plate in which the terminals are mounted with adequate insulation of transparent bakelite.

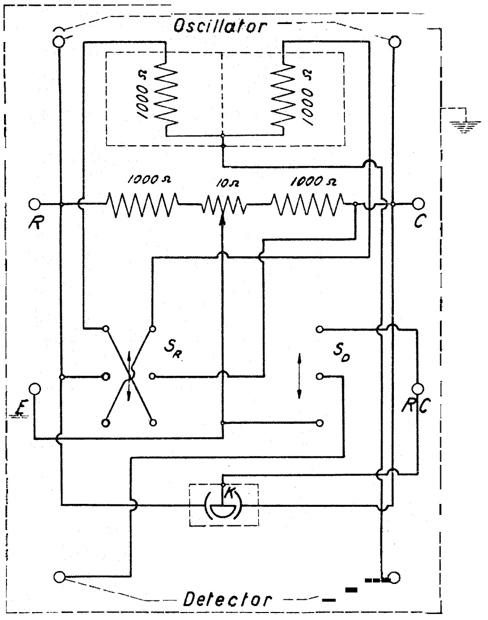

Fig. 5.

5. Measuring Resistance.—The resistance standard MB (Fig. 4) consists of three parts. A five-dial box of bifilar coils containing decades of 1/100, 1/10, 1, 10 and 100 ohm steps, is mounted in a shielded box. The screening in the box has a clearance of not less than 2.5 inches from any of the coils or contacts. This spacing proved to be sufficient by actual test to make the effect of the screen capacity on the resistance negligible for our purposes. The control knobs for operating the resistance dials are on the outside of the box, over a brass plate which forms a part of the shielding. They are fastened to the dials through stout bakelite rods. Complete shielding of these lower resistance dials as well as of the condenser K (Fig. 5) is of great convenience in entirely eliminating "hand effects" in measurements.

The effect of temperature on the resistance coils of higher values is not negligible in work requiring readings to 0.01 ohm and is not the same on every coil, so that corrections are not readily made. For this reason we found it desirable to control the temperature of the 1000-ohm step decade and the 10,000-ohm coils. These coils, of a woven type, forming one loop, are made by the Leeds and Northrup Co. They are practically reactance-free, compact and more constant in resistance than the card-wound type, being subject to very slight mechanical strain.

The 1000-ohm decade is mounted in air in a glass jar which is immersed in the metal shielded, oil-filled thermostat which holds the conductivity cell. The 10,000-ohm coils are mounted separately in large test-tubes, which are sufficiently spaced in a wooden frame, and also immersed in the thermostat. The 1000-ohm decade is permanently connected to the resistance box with a stiff heavy wire, avoiding close screening. The required connections in the thermostat, of the cell and measuring resistance are made with short heavy strands of bare copper wire through mercury cups. To avoid appreciable "dead end effects" the 10,000-ohm coils are appended one at a time as needed. Connections to the "bridge box" (Fig. 5) of the various units are made with flexible copper screened stranded wire, the screening being grounded.

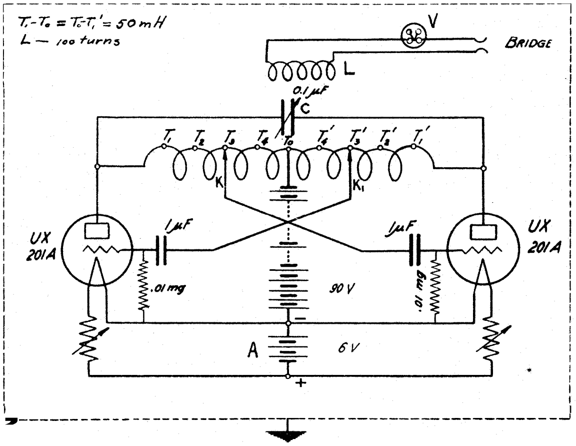

Fig. 6.

6. The Oscillator.—We are indebted to Dr. N. Frank of the Massachusetts Institute of Technology for furnishing us with the specification for an improved type of vacuum tube oscillator, designed by Eccles and Jordan. It consists of a double balanced oscillating circuit which has the advantage of giving an alternating current of very good wave form and of more constant frequency and intensity than that generated by the usual type of one-tube oscillator. The circuit is shown in Fig. 6. In varying the magnitude of the capacity C, which is made up of mica condensers which can be thrown in parallel by a system of switches (not shown in Fig. 6), the instrument can be made to give currents of frequencies ranging from about 600 to about 8000 cycles. The filament supply from the 6-volt storage battery **A** can be thrown on or off by means of a switch located near the bridge, so that the oscillator can be started or stopped conveniently during the measurements. The voltage supplied may be varied by looser coupling of the "pick up" coil L, or by changing the connections of K and K' to the taps T_1, T_2, T_3 and T_1', T_2', T_3', respectively. It is important to use separate batteries for the oscillator and detector circuits; otherwise, troublesome inductive couplings will occur. A calibrated vacuum thermocouple (V) is included in the apparatus for measuring the current supplied to the bridge.

7. Tests and Calibrations.—The resistance box, 100-ohm step decade, and the 10,000-ohm coils were calibrated with direct current against Bureau of Standards resistance standards, by the Carey Foster method, using an auxiliary resistance box. This was done directly with the bridge described above, using a high sensitivity galvanometer, and then checked on a well calibrated direct current Wheatstone bridge. The individual 10,000-ohm coils and various parallel combinations of them were also measured with the shielded bridge, at frequencies of 1000, 2000 and 3000 cycles, and with direct current. The variations from the direct current values obtained were less than 0.002% at 3000 cycles for 10,000 ohms, and entirely negligible at 1000 cycles, or for lower resistances.

The quality of the insulation, which is particularly important for the higher resistance measurements, was tested by connecting a 45-volt battery between the various binding posts, leads and screens, with a sensitive galvanometer in series. It was found to be well over 500 megohms across the important paths. The resistances of the metal contacts, important for the comparatively low resistance measurements, were also tested. A film of vaseline on the terminals and switch points made the resistance of the contacts reproducible and negligible (under 0.01 ohm).

In using the bridge, measurements are made by alternately adjusting R and K for the main balance, and W_R and W_K in the earthing circuit, with the detector in the correct position for each. The unknown and standard are then interchanged by throwing the reversed switch, and the procedure is repeated. The mean of the two readings gives the desired value.

No difficulty is found in making the adjustments, which may be made rapidly with a sensitivity of 0.001% directly without interpolation in measuring resistances of 1000 ohms or over. It is possible to use the bridge for measurements of high precision under conditions in which the use of an unshielded bridge would be quite difficult or impossible due to disturbances from other electrical circuits.

Measurements made with this bridge on the conductance of mixtures of potassium and sodium chlorides have already been reported.

The author wishes to express his gratitude to Dr. D. A. MacInnes for his helpful suggestions both during the progress of the work and in the preparation of the manuscript.

Summary

Part I. The theory of earth and shield capacity effects on alternating currents is discussed, and the results are applied to the Wheatstone bridge. The principles for the design of an electrostatically screened bridge for precision work are developed.

Part II. An alternating current, shielded bridge for precise electrolytic conductance measurements is described.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

A CONDUCTIVITY CELL FOR ELIMINATING ELECTRODE EFFECTS IN MEASUREMENTS OF ELECTROLYTIC CONDUCTANCE

BY THEODORE SHEDLOVSKY

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The electrolytic conductivity of a solution is ordinarily determined by measuring its resistance, with alternating current, in a cell previously calibrated with a solution having a known specific conductance. The product of this specific conductance and of the corresponding cell resistance is the "cell constant." Values of the specific conductance of other solutions are obtained by dividing the cell constant by the resistance measured in the cell.

Parker[1] has compared measurements on solutions of potassium chloride and hydrochloric acid, obtained in several cells over a range of concentrations. He found that determinations with different cells would lead to somewhat different conductance values. That is, there seemed to be an apparent variation in "cell constant" when the nature or concentration of the measured solutions was varied. Randall and Scott[2] found similar variations on measuring in two cells the conductance of solutions of several substances. These workers found very surprising variations, which in some cases were as high as 0.5%. Such large variations evidently make precision work impossible, and the following study was made with the purpose of eliminating them.

We have made a number of intercomparisons between several cells and have also observed apparent variations in cell constants, although considerably smaller ones than those found by the above investigators. In our work the variations were never greater than 0.2% with bright platinum electrodes, and were always under 0.1% with platinized electrodes. This smaller variation is due, we believe, to the fact that our measurements were made with a bridge[3] which gave readings free from certain sources of error possible in the arrangements these workers used.

Parker has suggested that the variations of cell constants are due to adsorption at the electrode. However, adsorption would be less on bright electrode surfaces, which, as we have just seen, give the largest variations. Therefore, adsorption cannot entirely account for the observations. In addition, the bridge readings with bright electrodes showed fluctuations of a nature suggesting variable polarization effects. Such fluctuations disappeared when the electrodes were lightly platinized, but it is quite pos-

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[1] Parker, THIS JOURNAL, 45, 1366, 2020 (1923).

[2] Randall and Scott, *ibid.*, 49, 636 (1927).

[3] Shedlovsky, *ibid.*, 52, 1793 (1930).

sible that such polarization was made constant by this procedure, rather than eliminated.

In this paper is described a cell which was designed for studying means of eliminating any effects at the electrodes which would disturb conductance measurements. The results of test measurements with the cell are also reported. To anticipate the conclusions, these results indicate that cell constant variations disappear if electrode effects are completely eliminated.

The Cell

The cell is shown diagrammatically in Fig. 1. It is provided with two end, or conducting, electrodes O and D, and the three loop, or detector, electrodes a, b and e. The electrodes O and D are hollow cones of platinum foil, made as nearly alike as possible, and a, b and c are loops of platinum wire. All the electrodes are sealed directly to the inner surface of the cell and are very lightly platinized. The cell is constructed from Jena glass 16^{III}, which may be sealed directly to platinum. This glass also has a very low solubility.

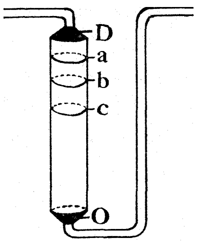

Fig. 1.

Such a cell may be connected into the Wheatstone bridge circuit in a number of different ways. For instance, measurements may be made in the ordinary manner between various electrode pairs. We have used the pairs OD, ab, bc, and ac in this way. This is obviously equivalent to an intercomparison between four ordinary cells. One of the purposes of this investigation was to see whether variations of the cell constant would disappear if similar electrodes were included in two arms of the bridge during measurement. The arrangement is shown in Fig. 2. It was hoped that the disturbing variations would be eliminated if measurements were made with one of the loop electrodes (a, b or c) connected to the detector, electrode O to one end of the current source, and the electrode D to a resistance box in the other arm of the bridge. Thus, for example, the portion of the cell (aO) with the electrode effect from O is balanced by the resistance box in series with the electrode effect from D, and the portion of the cell (aD) K is the condenser for balancing the resistances in the two arms, and the two 1000-ohm coils are the ratio arms. This particular arrangement we have called [a]. [b] and [c] are similar arrangements with the detector connected to (b) or (c) instead of to (a).

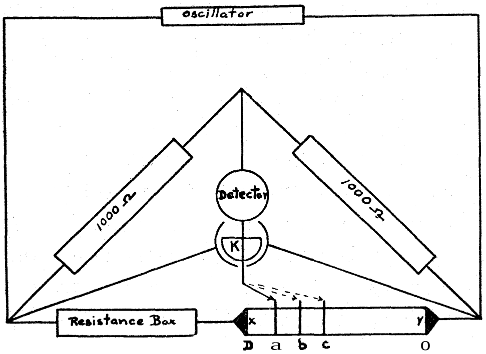

Fig. 2.

Parker,[1] who has made some excellent determinations of absolute conductance values for potassium chloride solutions, partially corrected for electrode effects by subtracting measurements made in two different cells provided with similar electrodes. He hoped that the electrode effect would be eliminated from the measurements if all determinations were made with the same two cells and the difference between the two readings were always taken as the resistance value. This would be so if the electrodes in the two cells behaved in exactly the same manner in all measurements. The method of making measurements by arrangements [a], [b] and [c] was chosen for obtaining directly the results given by Parker's two cell scheme. The difference between two of our measurements, ab, ac, bc, using the various pairs of loop electrodes as ordinary cells, corresponds to Parker's actual scheme. In Table II these arrangements are represented by (ac) (ab) and (ac)-(bc).

Referring once more to Fig. 2, let us call x the effect on the resistance due to the electrode D, and y the effect due to the electrode O. The current density at these electrodes depends on whether the detector is connected to a, b or c; that is, on the resistance between the detector electrode and the current source terminals, other things being equal. We found that a ten-fold change in current density attained by altering the voltage supplied to the bridge had no effect on the value of a particular measurement, so that it is fair to assume that x and y remain essentially the same whether the detector is connected to a, b or c. Let us call R_a, R_b, R_c the resistance box readings for the arrangements [a], [b] and [c], respectively. Since the loop or detector electrodes draw no current when the bridge is balanced, it seems plausible to assume that there is no effect at such electrodes that influences the readings.

We can write the following equations representing the conditions of balance in our bridge for the arrangements [a], [b] and [c]

$$\begin{array}{lll} [a] & R_a + x + \rho_{Da} = \rho_{oa} + y; & R_a = \rho_{oa} - \rho_{Da} + Y - x \\ [b] & R_b + x + \rho_{Db} = \rho_{ob} + y; & R_b = \rho_{ob} - \rho_{Db} + y - x \\ [c] & R_c + x + \rho_{Dc} = \rho_{ac} + y; & R_c = \rho_{ac} - \rho_{Dc} + y - x \end{array}$$

where ρ_{Da} is the resistance of the solution between D and a, etc. The actual reading observed, for instance R_a, corresponds to the difference between the two fixed portions of the solution Oa and Da, modified by the effects from the electrodes. If x = y, this method of measuring conductances is free from these electrode errors. However, if x and y are not equal, the electrode effects can be entirely eliminated by taking the difference between any two of the measurements [a], [b] and [c]. Thus

$$\begin{array}{ll} [a] - [b] & R_a - R_b = \rho_{oa} - \rho_{ob} + \rho_{Da} + \rho_{Db} = 2\rho_{ab} \\ [a] - [c] & R_a - R_c = 2\rho_{ac} \\ [b] - [c] & R_b - R_c = 2\rho_{bc} \end{array}$$

Thus, for instance, the difference $R_a - R_b$ is equal to twice the resistance of the solution between a and b, without error due to effects at the conducting electrodes.

The Measurements

Measurements were made with the cell described in the various ways discussed above. Four series were carried out at 1000, 2000 and 3000 cycles. First the cell was filled with potassium chloride solution (approx. 0.005 N) and then with three different concentrations of hydrochloric acid (approx. 0.001, 0.002 and 0.004 N). The cell was immersed in an oil thermostat which maintained a temperature regulation accurately to ±0.001°. The temperature was measured with a platinum resistance thermometer sensitive to about 0.0002°. A shielded bridge. described in another paper,[3] supplied with current from a balanced vacuum valve oscillator, and a detector amplifier was the measuring apparatus. 'She resistance box used in the measurements was calibrated to 0.01%.

The data are summarized in Tables I and II. The figures shown in Table I represent the resistances corresponding to the various arrangements when the cell was filled with approximately 0.005 N potassium

TABLE I

RESISTANCES WITH (APPROX.) 0.005 *N* POTASSIUM CHLORIDE

	1000 cycles	2000 cycles	3000 cycles
OD	8118 9	8118 9	8118.8
ab	1161.0	1160.6	1160.4
bc	1206 9	1206 A	1206.5
ac	2030 0	2029 6	2029.4
ac − ab	869.0	869.0	869.0
ac − bc	823.1	823.0	822.9
[a]	6064 3	6064.0	6063.6
[b]	4414.6	4414.4	4413.9
[c]	2705.8	2705.5	2705.1
[a] − [b]	1649.7	1649.6	1649.7
[a] − [c]	3358 5	3358.5	3358 5
[b] − [c]	1708.8	1708.9	1708.8

TABLE II

RESISTANCE RATIO VALUES

	Resistance HCl (concn.) / Resistance KCl (approx. 0.005 N)				Top value, 1000 cycles; middle value, 2000 cycles; bottom value, 3000 cycles	
	C = approx. 0 004 *N*	% error	*C* = approx. 0 002 *N*	% error	C = approx. 0 001 *N*	% error
	0.42605	−0.03	0.83440	−0.01	1.6763	−0.02
OD	.42605	− .03	.83437	− .02	1.6760	− .04
	,42604	− .03	.83437	− .02	1.6756	− .07
	....	....	.83437	− .02	1.6755	− .07
ab	,42618	+ .O1	.83448	....	1.6759	− .05
	,42620	+ .O1	.83454	....	1.6760	− .04
	....	....	.83429	− .02	I 6760	− .04
bc	.42616	....	.83441	− .01	1 6762	− .03
	,42619	+ .01	.83448	....	1.6763	− .02
	....	....	.83439	− .01	1 6760	− .04
ac	.42612	− .01	.83445	− .01	1.6762	− .03
	,42613	....	.83439	− .01	1.6764	− .02

TABLE II (*Concluded*)

	C = approx. 0.004 N	% error	C = approx. 0.002 N	% error	C = approx. 0.001 N	% error
		.	0.83437	−0.02	1.6767	....
ac − ab	0.42602	−0 03	.83437	− .02	1.6772	+0.03
	.42591	− 06	.83414	− .04	1.6768	....
	.42604	− .03	.8345	...	1.6761	− .04
ac − bc	.42604	− .03	.8345	....	1.6761	− .04
			.8342	− .03	1.6765	− .01
	.42599	− .04	.83438	− .01	1.6774	+ .04
[a]	.42601	− .03	.83440	− .01	1.6763	− .02
	.42604	− .03	.83442	− .01	1.6762	− .03
[b]	.42591	− .06	.83437	− .02	1.6762	− .03
	.42593	− .05	.83436	− .02	1.6761	− .04
	.42595	− .05	.83439	− .01	1.6760	− .04
	.42579	− .08	.83425	− .03	1.6760	− .04
[c]	.42584	− .07	.83426	− .03	1.6758	− .05
	.42590	− .06	.83428	− .03	1.6755	− .07
	.42618	+ .01	.83446	....	1.6767	....
[a] − [b]	.42618	+ .01	.83445	....	1.6767	....
	.42618	+ .01	.83448	....	1.6767	....
	.42615	....	.83450	....	1.6767	....
[a] − [c]	.42615	...	.83451	....	1.6767	....
	.42615	....	.83450	....	1.6767	....
	.42611	− .01	.83456	....	1.6767	....
[b] − [c]	.42611	− .01	.83452	....	1.6767	....
	.42610	− .01	.83454	....	1.6767	....
Correct value taken	.42615		.83450		1.6767	

chloride. Table II gives the corresponding resistance ratio, i. e., $R_{\text{HCl (c)}}/R_{\text{KCl (0.005 }N\text{, approx)}}$ for the three hydrochloric acid solutions measured. These values are, therefore, proportional to the specific resistance of the three hydrochloric acid solutions as obtained from the various types of measurements, after calibrating with a potassium chloride solution.

It is evident that the arrangements [a] − [b], [a] − [c], [b] − [c], which are free from conducting electrode effects, as shown above, give the most consistent values. These figures show practically no variations with frequency, nor of "cell constant," the average deviation being within 0.01%, which is the precision to which the resistance box is calibrated. We have, therefore, assumed as correct the values obtained by making measurements in this manner. The percentage error of the values obtained from the other arrangements on this basis is indicated in Table II to the nearest 0.01%.

Discussion

Since electrodes O and D were made as nearly alike as possible both in construction and in the subsequent platinizing, we should expect smaller variations in the arrangements [a], [b] and [c] in which these two electrodes are in opposite arms of the bridge than in the ordinary arrangement OD, if the cause of the variations is due to simple adsorption. This does not seem to be generally true, which suggests that besides adsorption there is superimposed another effect. Referring to the equations [a], [b] and [c], the results seem to indicate that x and y may have opposite signs, so that their effect on the measurements may increase instead of decreasing when they appear in opposite branches of the bridge. Such may be the case if there is a definite difference between the rates of building up and decaying of the e. m. f. at the electrode surfaces for the oxidation and reduction parts of the current cycle.

It appears from our results that conductance values, free from errors due to effects at electrodes which tend to change the apparent cell constant, can be obtained with a four electrode cell. The measurements for the arrangements [a] – [b], [a] – [c] and [b] – [c] represent a comparison between three such four electrode cells and lead to consistent conductance values.

Cells of the ordinary type (with two electrodes), which may be more convenient for routine work, can be calibrated by comparison with a four electrode cell.

Summary

1. A multiple electrode cell for studying the elimination of electrode effects in conductance measurements is described.

2. Data obtained with one potassium chloride solution and three hydrochloric acid solutions of different concentrations, using various measuring arrangements of electrodes, are given for three frequencies.

3. The assumption of adsorption at the electrodes does not entirely explain the variations in "cell constant" which are observed.

4. A four electrode arrangement is found to give consistent results at the three frequencies without variations in "cell constant."

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF AMERICAN UNIVERSITY]

THE USE OF ORTHO,PARA-DIHYDROXY-AZO-PARA-NITROBENZENE AS A TEST FOR THE MAGNESIUM ION

BY EDWARD WILLIAM ENGEL

RECEIVED DECEMBER 26, 1929 PUBLISHED MAY 8, 1930

The azo dye *o,p*-dihydroxy-azo-*p*-nitrobenzene has been reported by K. Suitsu and K. Okuma[1] as rendering a very sensitive test for the magnesium ion. A recently published note by Ruigh[2] gives the method of preparation and use. A 0.5% solution of the dye in 1% sodium hydroxide solution is stated to be the proper concentration to employ. The test depends upon the formation of a blue lake with the azo dye in dilute sodium hydroxide solution. It is also stated that ammonium salts render the test less sensitive, while the presence of nickel or cobalt, cations which form similar lakes with the dye, invalidates or confuses the test.

Numerous tests with this reagent have been made in this Laboratory, and it is believed that a more sensitive and more convenient method for its use has been developed. In addition, this usage has the advantage of being very simply conducted and, with very few exceptions, can be carried out, if desired, without the preliminary, time-consuming removal of interfering anions or cations. The classical magnesium ammonium phosphate method of determining magnesium is often confusing, inasmuch as aluminum hydroxide, silicic acid, strontium phosphate and calcium phosphate often precipitate at this point in the ordinary qualitative analysis schemes. Methods of removing these substances usually involve several time-consuming separations which are, in addition, generally not very sensitive.

'She method which was found to be the most practicable, involves the evaporation of the unknown solution to a small volume, or to dryness if the quantity of magnesium is very small and if substances such as organic material (which would char under such treatment) are absent. A clean porcelain crucible is essential for this test and the evaporation should be conducted within it. Five or ten ml. of 6 *N* sodium hydroxide is now added to the porcelain crucible or casserole and finally one drop of the dye reagent. In about ten seconds or more, depending upon the concentration of the magnesium ion, a light blue stain will appear upon those portions of the casserole which had been in contact with the solution containing magnesium. This stain adheres quite tenaciously to the surface of the casserole. If the supernatant liquid is now poured from the casserole and the stain washed twice with 5 to 10 ml. of water, the stain turns green in color but does not disappear. If the same test is carried out with nickel alone, the stain does not form as rapidly, adheres less tenaciously and turns red-

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[1] **Suitsu** and **Okuma,** *J. Soc. Chem. Ind.* Japan, 29, 132–138 (1926); C. *A.* **20,** 3000 (1926).

[2] Ruigh, THIS JOURNAL, **51,** 1456–1457 (1929).

brown in color upon washing with water. If a similar procedure is followed with cobalt, no stain whatever forms, although a blue lake will appear.

Treatment of the stains with concentrated ammonium hydroxide is also characteristic. In the case of magnesium, the stain is not affected, but in the case of nickel the stain dissolves readily. If desired, this solution could be tested for nickel in the usual manner, that is, by the addition of dimethylglyoxime to the solution with the formation of a precipitate of nickel dimethylglyoxime.

Quantitative investigation indicates that in the absence of de-sensitizing material, 3×10^{-6} g. of magnesium can be readily detected with this technique. If, therefore, the magnesium test is applied in its customary place in the fourth or fifth group of the commonly employed qualitative analysis schemes, this small quantity of magnesium will be capable of detection.

Experiments were also conducted to determine the validity of this test in the presence of the cations commonly met with in qualitative analysis either tested singly or in any possible combination. In the presence of these cations, tested individually, no interference in any case was obtained. A great many combinations were tested, and, in general, any grouping of cations which form colored precipitates (particularly blue precipitates) upon the addition of sodium hydroxide, renders the test somewhat uncertain. Portunately, however, only a few such conflicting combinations were found. Copper and aluminum illustrate a case in point, the cupric hydroxide apparently being absorbed by the aluminum hydroxide, thereby forming a cbnfusing lake not readily soluble in concentrated ammonium hydroxide.

Further investigation indicates that acetates, tartrates and ammonium salts render the test less sensitive but that if magnesium be present in sufficient quantity (and in the case of organic material such as tartrates) evaporation is not carried to complete dryness (to prevent charring), the test is still valid. The quantity of these conflicting substances determines, quite naturally, the amount of detectable magnesium. Quantitative tests show that with 1 g. of these substances present only 3×10^{-4} g. of magnesium can be detected. Consequently, when great sensitivity is required, organic matter and ammonium salts should be first removed and the solution then evaporated to dryness before applying the stain method technique.

Summary

A new technique for the use of *o,p*-dihydroxy-azo-*p*-nitrobenzene as a test for the magnesium ion has been described.

With this technique the test is valid in the presence of any one of all of the common cations met with in qualitative analysis and in a ***great*** many combinations of these cations.

Nickel, cobalt or both do not confuse the test.

Acetates, tartrates and ammonium salts do not interfere but decrease the sensitivity of the test.

The test can be used most efficiently as a substitute for the classical magnesium ammonium phosphate test commonly employed in qualitative analysis procedures. Used in this way, 3×10^{-6} g. of magnesium can be detected.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE INTERPRETATION OF THE COLLIGATIVE PROPERTIES OF WEAK ELECTROLYTES

BY MERLE RANDALL AND CLYVE ALLEN

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Introduction

Although the importance, in the study of solutions, of the activities or activity coefficients[1,2] of the components has been most emphasized in the field of strong electrolytes, these quantities are, of course, of no less importance to the study of weak electrolytes and of non-electrolytes. Moreover, although the methods of determining the activity coefficients[1,2] have been most widely studied in the case of strong electrolytes, these methods are, of course, equally applicable to weak electrolytes and non-electrolytes. The application of these methods is illustrated by the work of Randall and Failey[3] in determining the activity coefficients of gases, of non-electrolytes, and of the undissociated part of weak electrolytes in solutions of electrolytes.

In the study of electrolytes it has been customary to regard as strong those completely or practically completely dissociated in dilute aqueous solution, and as weak those incompletely dissociated at finite concentrations. The question as to the actual extent of dissociation of a strong electrolyte in a given solution is of importance from a kinetic standpoint and has received considerable attention. To account for apparent evidences of incomplete dissociation of strong electrolytes consisting of small ions or those having "un-centrally located charges," Bjerrum[4] suggested a modification of the inter-ionic attraction theory of Debye and Hückel[5] whereby such ions, of opposite charge, when closer together than a certain minimum distance (dependent upon the dielectric constant of the medium and the absolute temperature) would be regarded as associated—behaving

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, Chapters XXII to XXVIII.

[2] Randall, *Trans. Faraday Soc.*, 23, 498, 502 (1927).

[3] (a) Randall and Failey, *Chem. Reviews*, 4, 271, 285, 391 (1927); see also (b) Livingston, THIS JOURNAL, 48, 45 (1926).

[4] Bjerrum, *Det. Kgl. Danske Videnskab. Selskeb. Math.-fys. Medd.*, 7, No. 9 (1926).

[5] Debye and Hückel, *Physik. Z.*, 24, 185 (1923).

osmotically as though undissociated. Mueller,[6] Gronwall,[7] and, more recently, Gronwall, LaMer and Sandved,[8] have shown, however, that Bjerrum's practical results can be explained by a more thorough consideration of the postulates of Debye and Hückel.

Whether or not we consider an electrolyte as completely dissociated, especially for thermodynamic treatment, is largely a matter of convenience. For example, it has been convenient for a long time to consider such substances as ammonium hydroxide, acetic acid and mercuric chloride as mostly undissociated in solution and to consider a definite equilibrium between the ions and undissociated portions. On the other hand, with substances as strong as dichloro-acetic acid it is perhaps more convenient to consider them strong electrolytes but having activity coefficients less than those of the typically strong electrolytes.

It is not the purpose of this paper to discuss the colligative properties of weak electrolytes on the basis of any particular mechanistic theory, but rather to indicate methods whereby the activity of weak electrolytes may be calculated from measurements of the activity of the solvent, and to clarify our conceptions of the thermodynamic treatment of "so-called" incompletely dissociated substances.

Theoretical

For clearness we shall confine our discussion entirely to an aqueous solution of a univalent electrolyte. We shall use the symbols employed by Lewis and Randall[1] and by Randall and Failey.[3]

The stoichiometrical molality of the electrolyte will be denoted by m, the molality of the undissociated portion by m_u, that of the negative ion by m_- and that of the positive by m_+; a_u, a_- and a_+ will represent the corresponding activities, and a_1 that of the solvent. Also we will for simplicity call $m_+ = m_- = m_\pm$, so that $m = m_u + m_\pm$ and call $m_\pm/m = \alpha$, the degree of dissociation in the usual sense.

Now, if we use the basis of treatment which we have used for strong electrolytes,[1,2] the activity of the solute, a_2, is equal to the product a_+a_-, or $a_\pm = a_2^{1/2}$. For slightly weak electrolytes, or weak electrolytes at very low concentrations (if the effect of the ions of the solvent upon the dissociation is neglected), the activity of the solute is more nearly equal to the square of the mean molality of the ions than to the molality of the undissociated substance.

We therefore define the following activity coefficients:

$$\gamma_0 = a_2/m, \quad \gamma = a_2^{1/2}/m, \quad \gamma_u = a_u/m_u, \quad \gamma_\pm = a_\pm/m_\pm$$

where γ_0 is the stoichiometrical activity coefficient of a solute considered as undissociated; γ is the stoichiometrical activity coefficient of a univalent

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[6] Mueller, (a) *Physik. Z.*, 28, 324 (1927); (b) 29, 78 (1928).

[7] Gronwall, *Proc. Nat. Acad. Sci.*, 13, 198 (1927).

[8] Gronwall, LaMer and Sandved, *Physik. Z.*, 29, 358 (1928).

electrolyte, regardless of whether or not the electrolyte is completely dissociated, and, moreover, by our conventions, is the stoichiometrical mean activity coefficient of the ions; γ_u is the activity coefficient of the undissociated portion of the solute, and $\gamma_{\pm}$ the mean activity coefficient of the ions. By these definitions

$$\gamma \equiv \alpha\gamma_{\pm}; \;\; \log \gamma = \log \alpha + \log \gamma_{\pm} \qquad (1)$$

By virtue of the rapid interconvertibility of the solute constituents, we have also the relation[1]

$$\mathrm{HA} = \mathrm{H}^+ + \mathrm{A}^-; \;\; K = a_{\pm}{}^2/a_u \qquad (2)$$

where K is the dissociation constant.

For an aqueous solution of a binary electrolyte, the general partial molal equation[1] in the form

$$m\, d\ln a_2 = -55.51\, d \ln a_1 \qquad (3)$$

is equivalent to

$$d \ln \gamma_0 = -(55.51/m)\, d \ln a_1 - d\, m/m \qquad (4)$$
$$d \ln \gamma = -(55.51/2m) d \ln a_1 - d\, m/m \qquad (5)$$

At the freezing point of the solution, these equations become[1]

$$\mathrm{d} \ln \gamma_0 = \mathrm{d}\,\theta/\lambda m + \theta\, \mathrm{d}\,\theta/\lambda'' m + \ldots - \mathrm{d}\, m/m \qquad (6)$$
$$\mathrm{d} \ln \gamma = \mathrm{d}\,\theta/2\lambda m + \theta\, \mathrm{d}\,\theta/2\lambda'' m + \cdots - \mathrm{d}\, m/m \qquad (7)$$

where $\lambda = 1.858$ and $\lambda'' = (0.00057)^{-1}$ are constants, and θ is the freezing point lowering.

Introducing the Lewis and Randall divergence functions[1]

$$1 - \theta/\lambda m = j_1, \; (\nu = 1) \text{ and } 1 - \theta/2\lambda m = j_2, \; (\nu = 2)$$

and integrating, we have

$$n\, (\gamma_0/\gamma_0') = -(j_1 - j_1') - \int_{m'}^{m} (j_1/m) \mathrm{d}\, m - \int_{m'}^{m} (\theta/\lambda'' m) \mathrm{d}\,\theta \ldots \qquad (8)$$

and, following Randall and White[9]

$$\ln\, (\gamma/\gamma') = -(j_2 - j_2') - 2\int_{m'}^{m} (j_2/m^{1/2})\, \mathrm{d}\, m^{1/2} - \int_{m'}^{m} (\theta/2\lambda'' m)\, \mathrm{d}\,\theta \qquad (9)$$

For a binary electrolyte at infinite dilution

$$\underset{m \to 0}{\text{Limit}}\, (a_2/m^2) = 1; \;\; \underset{m \to 0}{\text{Limit}}\, (\gamma_0/m) = 1; \;\; \underset{m \to 0}{\text{Limit}}\, (\gamma) = 1 \qquad (10)$$

By definition, if we wish to use the quantity γ_0 in a region in which the divergence function using $\nu = 1$ is most convenient, we may refer γ_0 to a proper standard state by the relation

$$\log \gamma_0 = \log\, (\gamma)^2 + \log m \qquad (11)$$

and where we wish to use the quantity γ, in the region in which $\nu = 2$ is most convenient, we have

$$\log \gamma = -0.4343\, [j_2 + 2\int_{0}^{m} (j_2/m^{1/2})\, \mathrm{d}\, m^{1/2} + \int_{0}^{m} (\theta/2\lambda'' m)\, \mathrm{d}\,\theta + \cdots] \qquad (12)$$

Equation 12 may be easily evaluated by means of Equation 1 if we also know the α, $\gamma_{\pm}$ and m relations (in dilute solutions).

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[9] Randall and White, This Journal, 48, 2514 (1926).

Application of Foregoing Considerations.—Our correlation of γ_u, $\gamma_\pm$ and α with the empirical freezing point lowering equations of Lewis and Randall is to facilitate the treatment, in certain cases, of weak electrolytes in very dilute solution. Similar relations, of course, hold for the generalized divergence function of Randall and White.[2,9] Moreover, it is fully as important as in the case of strong electrolytes to adopt a consistent and logical standard state for the activity of weak electrolytes. (Values of quantities proportional to the activity coefficients have recently been obtained for several weak acids[10] by measurements of the freezing point lowering in concentrated solution. These quantities were given on the basis of an activity coefficient equal to unity in one molal solution. Such a standard state is not to be recommended and must ultimately cause confusion.) It is our immediate purpose to show that, on the basis of complete dissociation of the electrolyte at infinite dilution, we may evaluate the activity coefficients of weak electrolytes in dilute solution and that where K is known this is facilitated.

To this end we shall examine the consequences of two postulates: (1) that the mean activity coefficient of the ions of a partially dissociated univalent electrolyte at small molalities is the same as that of hydrochloric acid[11] at the same ionic strength and that the activity coefficient of the acid would not be considerably affected by the presence of small amounts of undissociated substance. (If the effect on the dielectric constant of dilute hydrochloric acid due to small additions of non-electrolyte were thought considerable, it could, of course, be corrected for on the basis of the interionic attraction theory.)

(2) That in sufficiently dilute solution the freezing point lowering or other similar colligative property due to the ions, $2\theta_i$, is the same as it would be if the undissociated part were not present; that the freezing point lowering of the undissociated part, θ_u, is the same as that if the dissociated part were not present, and that the total freezing point lowering is the sum of these two quantities.

The validity of Assumption 1 has to a large extent been demonstrated,[3] by methods which give directly the activity of the solute. If, as Randall and Failey found, the quotient, logarithm of activity coefficient of undissociated part of weak electrolyte by ionic strength, is approximately constant for weak electrolytes in salt solutions (the constant varies with the weak electrolyte or salt being considered), then in sufficiently dilute solution

$$(\ln \gamma_u)/\mu = k', \quad \gamma_u = e^{\mu k'} = 1 + \mu k' + (\mu k')^2/2 + \ldots \doteq 1 \qquad (13)$$

Furthermore, we offer here the possibility of verification of Assumption 2 by a correlation of the activity of the undissociated portion of an electrolyte with the activity of the solvent.

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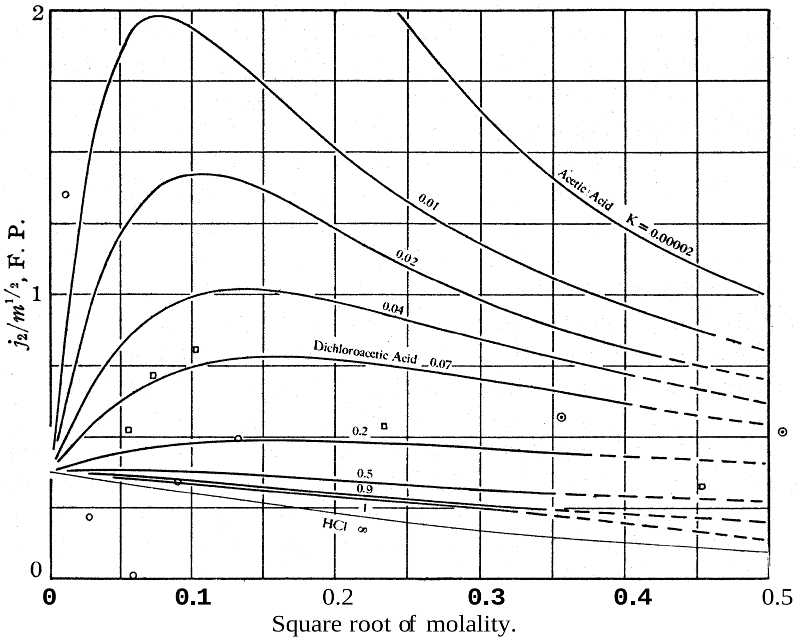
[10] Jones and Bury, Phil. Mag., [7] 4, 841 (1927).

[11] For bases we would take sodium hydroxide as a type strong base.

Inasmuch as the apparent dissociation constant from conductivity measurements, extrapolated to infinite dilution, K_A°, must be equal[1] to K (the correct interpretation[12,13] of α will give us K) we are frequently in *a* position to utilize this quantity, by the relations developed in the present section, to evaluate activity coefficients of weak electrolytes from measurements which give directly the activity of the solvent.[14]



○, Hausrath; ⊡ Wildermann, ⊙, Petersen.

Fig. 1.—Freezing point function for weak univalent electrolytes of various dissociation constants and for dichloro-acetic acid.

The curves of Fig. 1 were prepared from Randall and Young's[15] plots of the activity coefficient of hydrochloric acid at 0°. Knowing the true dissociation constant, $K = a_{\pm}^2/a_u$, of any univalent electrolyte, we may calculate the molality of the electrolyte corresponding to given values of ionic strength and ionic activity coefficients in the region where $\gamma_u = 1$, i. e.

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[12] Sherrill and Noyes, THIS JOURNAL, 48,1861 (1926).

[13] MacInnes, *ibid.*, 48,2068 (1926).

[14] The following experimental methods all give the activity of the solvent: freezing point lowering, vapor pressure lowering, boiling point raising, osmotic pressure, "dew-point" lowering, distribution ratio of the solvent and, in the case of a few solvents, measurements of the electromotive force in which the solvent is the substance involved in the electrode reactions. See Ref. 2.

[15] Randall and Young, THIS JOURNAL, 50,989 (1928).

$$K = (\gamma_{\pm}m_{\pm})^2/\gamma_u m_u \doteq (\gamma_{\pm}m_{\pm})^2/m_u; \ m_u = (\gamma_{\pm}m_{\pm})^2/K;$$
$$m \doteq m_{\pm} + (\gamma_{\pm}m_{\pm})^2/K \quad (14)$$

Although we use the assumption that the freezing point lowering caused by the undissociated part is the same as that of a perfect solution

$$\theta = 28, + 8, \doteq 28, + \lambda m_u \quad (15)$$

j_1, j_2, etc., are independent of this assumption.

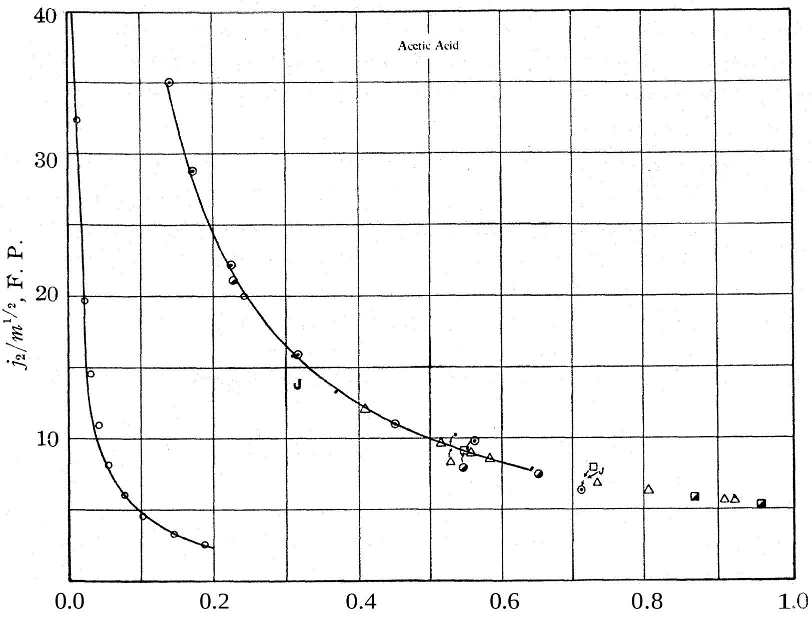

Fig. 2.—Freezing point function for acetic acid. ○ Hausrath, ◐ Jahn, A Jones and Bury, J Jones and Getman, □ Kendall, ◪ Kendall and King, ◉ Ostwald, • Roth.

In Figs. 1 and 2 are given the plots of $j_2/m^{1/2}$ thus calculated for univalent electrolytes of various dissociation constants.

In Fig. 1 we have also placed the points, $j_2/m^{1/2}$, calculated from the data of three investigators,[16] of the freezing point lowering of dichloroacetic acid. These points are evidently in very poor agreement among themselves. According to the dissociation constant at 18°, K_{291} = 0.0583,[17] and the heat of dissociation given by Steinwehr,[18] K_{273}, should be approximately 0.07. In cases of this sort, where the freezing point data

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[16] (a) Hausrath, *Ann. Physik*, [4] 9, 522 (1902); (b) Petersen, *Z. physik. Chem.*, 11, 174 (1893); (c) Wildermann, *ibid.*, IS, 337 (1894); (d) *ibid.*, 19, 233 (1894).

[17] Schreiner, *Z. anorg. allgem. Chem.*, 122,201 (1922).

[18] Steinwehr, *Z. physik.* Chem., 38, *185* (1901).

are very discordant, curves of this type serve to indicate the probable accuracy of the data.

In Fig. 2 are given the points, $j_2/m^{1/2}$, calculated from all the available data[19] of the freezing point lowering of acetic acid. These points show excellent agreement among themselves and, in turn, lie very closely along the curve for $K = 2 \times 10^{-5}$, which according to the extrapolation by Lewis and Randall of the data of Noyes and Cooper,[20] very likely represents the true K of acetic acid within 4 or 5%.

The curves of j_1/m for weak electrolytes are not given, as these, of course, rapidly approach extreme negative values in dilute solution, as is always the case when the value of ν assigned the substance is less than the true value (see Randall and Cann).[21]

Regarding the sharp peaks shown in the $j_2/m^{1/2}$ curves for weak electrolytes of low dissociation constant,[22] we see from our previous discussion that in just the region where they manifest themselves and graphical integration becomes laborious (very dilute solution) we may place most confidence in our postulates.

According to our discussion, we should have the relations

$$\log (\alpha\gamma_{\pm}/\alpha'\gamma_{\pm}') = -0.4343\left[(j_2 - j_2') + 2\int_{m'}^{m} (j_2/m^{1/2})\text{d}\, m^{1/2}\right] \qquad (16)$$

and

$$\log \alpha\gamma_{\pm} = -0.4343\left[j_2 + 2\int_{0}^{m} (j_2/m^{1/2})\text{d}\, m^{1/2}\right] \qquad (17)$$

true in very dilute solution where the integral of the θ term is negligible and our postulates should almost certainly be valid. As we have drawn our curves of Figs. 1 and 2 from our values of $m_{\pm}$, $\gamma_{\pm}$ and θ_i, and m's calculated from the K's, satisfaction of Equations 16 and 17 in these cases is, of course, to be expected.

Higher accuracy in determining the activity coefficients of weak electrolytes from freezing point lowering data is to be gained by higher accuracy in the values of the dissociation constant at 0°, as well as in the freezing point measurements.

The values of γ_0 and γ for acetic acid at round values of $m^{1/2}$ at the freezing point are given in Table I.

It will be noted that the values of γ_0 are very near the value of K, namely, 2×10^{-5}. The quotient γ_0/K given in the third column of the table shows

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[19] (a) Hausrath, Ref. 16a; (b) Jahn, *Ann. Physik. Chem*, [3] 60, 119 (1897); (c) Jones and Bury, Ref. 10; (d) Jones and Getman, *Am. Chem. J.*, *30*, 198 (1903); (e) Kendall, This Journal, 39, 2318 (1917); (f) Kendall and King, *J. Chem. Soc.*, 127, 1380 (1925); (g) Ostwald, *Z. physik. Chem.*, 75, 278 (1898).

[20] Noyes and Cooper, *Pub. Carnegie Inst.*, No. 63 (1907).

[21] Randall and Cann, This Journal, 50, 347 (1928).

[22] It is a characteristic of the curves of Fig. 1 that the maximum appears in more and more dilute solution the smaller the value of K.

TABLE I

THE ACTIVITY COEFFICIENT OF AQUEOUS ACETIC ACID AT THE FREEZING POINT

$m^{1/2}$	$\gamma_0 \times 10^5$	γ_0/K	γ
0.1	1.910	0.955	0.0440
.15	1.940	.970	.0295
.2	1.956	.978	.0220
.25	1.964	.982	.0175
.3	1.970	.985	.0143
.35	1.974	.987	.0121
.4	1.976	.988	.0108

that in solutions as strong as 0.1 M the effect of ionization of the acid may be disregarded. The quotient is easily interpolated and convenient for this purpose. When using this value of γ_0, however, we in effect make the same convention as in the case of a strong electrolyte, namely, that the standard state of aqueous acetic acid is one which is defined by the infinitely dilute solution; moreover, it is so defined that the standard free energy of the aqueous acid is the same as the sum of the free energies of the ions. The value of γ is as is to be expected very nearly the value of the degree of dissociation as ordinarily used, being the product of this quantity and $\gamma_\pm$, the activity coefficient. Since the effective ionic strength is very small, $\gamma_\pm$ is nearly unity.

It will be seen that the effect of our definitions is to make a distinction between the quantities γ and $\gamma_\pm$ as formerly employed by Lewis and Randall, who made these quantities as well as m and $m_\pm$ identical for a univalent electrolyte. We have retained that part of their convention which makes the activity of the solute the geometrical product of the activities of the ions.

Regarding the possibility of testing the validity of the assumption $\gamma_u = 1$ from measurements of the activity of the solvent, we should be able to subtract the calculated quantity $2\theta_i$ from observed freezing point depressions, form the function $j_u/m_u = [1 - (\theta_u/\lambda m_u)]/m_u$ and examine its approach to constancy in dilute solution. (A plot of $2\theta_i$ and $m_\pm$ against m for the electrolyte studied, K = 2.0×10^{-5} in this example, is useful for the purpose.)

Table II shows j_u/m_u for acetic acid, calculated from the data of Hausrath[16a,23] and Jones and Bury,[19c] probably as accurate data as any in existence in their respective ranges of molality. The values are of the expected order of magnitude[3a] (see Equation 13) except in the most dilute solutions. Such a test is exacting and enormously magnifies the experimental errors.[24]

It might be pointed out that our postulates have intrinsically rather a wide field of applicability. That is, the assumption that the ions of weak

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[23] Hausrath, *Ann. Physik,* [4]**9,** 548 (1902).

[24] For the purposes of this paper we may neglect the common ion from the solvent.

TABLE II

VALUES OF j_u/m_u FOR AQUEOUS ACETIC ACID

m	θ	m_u	j_u/m_u	Author
0.001749	0.003522	0.001569	−14.357	Hausrath[16a,23]
.003007	.006062	.002767	−1.352	Hausrath[16a,23]
.005902	.01172	.005562	−1.899	Hausrath[16a,23]
.01048	.02061	.01002	−1.501	Hausrath[16a,23]
.02082	.04035	.02017	−0.589	Hausrath[16a,23]
.03535	.06839	.03449	− .502	Hausrath[16a,23]
.05876	.11124	.05765	− .00509	Hausrath[16a,23]
.1669	.314	.1650	− ,00899	Jones and Bury[Lg0]
.2653	.497	.2629	+ .00201	Jones and Bury[19o]
.2811	.526	.2786	.00520	Jones and Bury[Lg"]
.3097	.578	.3071	.01202	Jones and Bury[L9"]
.3401	.636	.3374	.00373	Jones and Bury[19o]
.5432	1.002	.5397	.02480	Jones and Bury[Lg0]
.6514	1.197	.6476	.02575	Jones and Bury[19o]

electrolytes act like those of hydrochloric acid (at the same ion molality) makes little difference in electrolytes of K < 0.01, because the important thing is how far the undissociated portion departs from the ideal. On the other hand, with electrolytes of K > 0.5, the assumption of $\gamma_u = 1$ makes little difference. Of course, such assumptions should not be employed and are not needed except in quite dilute solution. Our postulates appear to be very nearly valid in the case of acetic acid up to about 0.4 M, far beyond the range in which they are needed.

Curves of the type shown in Fig. 1, in addition to serving as a criterion for the accuracy of data, may also be employed for the detection of and estimation of the degree of dissociation. Inasmuch as freezing point measurements are frequently not dependable in solutions more dilute than 0.01 M, we may employ a simple modification of the curves of Fig. 1 as an aid in evaluating divergence functions in more dilute solutions. For example, values of $j_2/m^{1/2}$ at m = 0.01 (Fig. 1 and Table III) are plotted against log K as illustrated in Fig. 3, giving us a plot whereby we may determine probable values of K from a single value of the freezing point lowering at 0.01 M. Thus if we have a single measurement

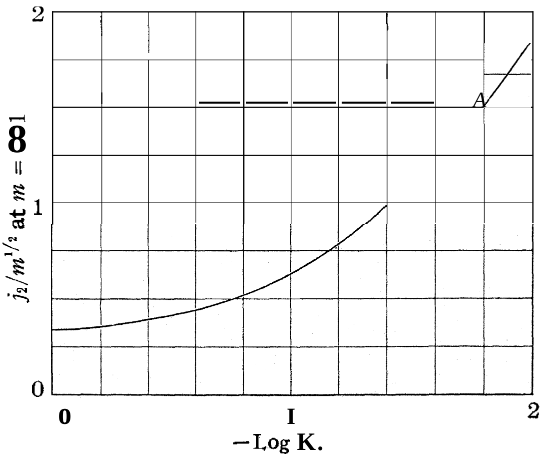

Fig. 3.—Freezing point function at 0.01 M for univalent acids of various dissociation constants.

of the freezing point at 0.01 *M*, we may calculate the value of $j_2/m^{1/2}$ and by interpolation along the curve of **Fig. 3** we find the value of log K, or, having K, may complete the divergence function in the very dilute range. This method is most valuable in the range of $K > 10^{-3}$.

TABLE III

STOICHIOMETRIC ACTIVITY COEFFICIENTS OF WEAK ACIDS AT $m = 0.01$

K	$m_\pm$ at $m = 0.01$	$\gamma_\pm$	$m_\pm/m$	γ	$j_2/m^{1/2}$
0.9	0.0099	0.907	0.99	0.898	0.343
.2	.0094	.909	.94	.854	.479
.07	.0090	.910	.90	.819	.747
.04	.0084	.913	.84	.767	,993
.02	,0075	.917	.75	.687	1.425
.01	.0065	.921	.65	.599	1.935
2×10^{-5}	.0005	.975	.05	.044	4.85

Summary

The methods of Lewis and Randall for determining activity coefficients from freezing point measurements or from other measurements of the activity of the solvent are formally reviewed for weak univalent electrolytes.

The logarithm of the activity coefficient of a weak electrolyte (basis of strong electrolytes) is equal to the sum of the logarithm of the degree of dissociation and the logarithm of the activity coefficient of the ions as such.

Use of the dissociation constant, $K = a_\pm^2/a_u$, in evaluating the divergence functions of weak electrolytes in very dilute solution is introduced.

The procedure to be followed in determining the activity coefficient of acetic acid in dilute solution from measurements of the activity of the solvent is shown as an example of the treatment of a typical weak electrolyte.

In dealing with weak electrolytes it is expedient to have an easily interpolated activity coefficient for employment where dissociation is inappreciable and one for use where dissociation is considerable. These should be thermodynamically related and should permit of evaluation in very dilute solution. In addition, these coefficients should reduce in the limiting cases, on the one hand to the activity coefficient of a non-electrolyte, and on the other to that of a completely dissociated electrolyte. They should also be defined so that the reference solution is the same for solvent and solute. These requirements are entirely satisfied by the methods described in this paper.

A method of determining the dissociation constant of moderately weak electrolytes from a single measurement of the freezing point at 0.01 *M* is given.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. VIII. ACETIC AND BUTYRIC ACIDS

BY C. P. SMYTH AND H. E. ROGERS

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The fatty acids have been so extensively investigated from many points of view that their dielectric behavior should be of unusual interest. Solutions of acetic acid in benzene and in ether were studied some years ago by Dr. S. O. Morgan and one of the writers, but, as the results were peculiar and as some doubt arose as to the purity of the acetic acid which had been employed, no use was made of the data. The measurements have been repeated with carefully purified acetic acid over a wider range of temperature and extended to butyric acid. The apparatus, with which the dielectric constant was determined at a wave length of 600 meters, has been described previously.[1]

Preparation of Materials

Benzene.—Benzene was purified in the usual manner, being finally dried and distilled over sodium; b. p. 80.1°; n_D^{20} 1.50135.

Ether.—U. S. P. ether was shaken several times with a strong sodium chloride solution containing a little sodium hydroxide, washed with water, dried over calcium chloride and distilled; b. p. 35.1°; d_4^{20} 0.7137.

Acetic Acid.—Merck's C. P. glacial acetic acid was crystallized twelve times, the final melting point being 16.6° and the refractive index n_D^{20} 1.37175. This sample was fractionally distilled; b. p. 117.8°; d_4^{20} 1.0491; n_D^{20} 1.37175.

Butyric Acid.—n-Butyric acid obtained from the Eastman Kodak Company was fractionally distilled, the fraction boiling between 163.2 and 163.4° being taken for the measurements; d_4^{20} 0.9591.

Experimental Results

For the acetic acid solutions and the pure substance the dielectric constants ϵ were measured at temperature intervals of approximately 10° and the densities d at intervals of about 15°. The values given for them in Table I were obtained by graphical interpolation. The butyric acid measurements were made at three fixed temperatures, which make interpolation unnecessary. The polarizations, P_2, of the acids were calculated by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{c_1M_1 + c_2M_2}{d} \text{ and } P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2, and P_1 and P_2 are, respectively, the mole fractions, molecular weights, and polarizations of the individual components.

In the case of pure acetic acid slightly supercooled to 16.4°, a resistance

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[1] Smyth, Morgan and Boyce, THIS JOURNAL, 50,1536 (1928); Smyth and Morgan, *ibid.*, 50, 1547 (1928).

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AND POLARIZATIONS OF ACIDS

Benzene–Acetic Acid

Mole fr. CH_3COOH = t, °C.	0	0 0978	0 2305	0.4372	0 6134	0 7912	1 000
0	2.336	2.375	2.464	2.706	3.113	3.956	
10	2.315	2.358	2.449	2.700	3.118	3.981	6.074
20	2.295	2.340	2.434	2.693	3.124	4.007	6.13
30	2.274	2.322	2.418	2.687	3.130	4.032	6.20
40	2.253	2.303	2.403	2.679	3.133	4.052	6.27
50	2.232	2.285	2.388	2.672	3.132	4.067	6.36
60	2.210	2.266	2.372	2.663	3.129	4.078	6.47
70	2.188	2.246	2.357	2.655	3.126	4.084	6.60
				d			
0	0.8986	0.9100	0.9222	0.9484	0.9760	1.0134	
10	.8896	.8989	.9113	.9369	.9645	1.0020	1.0607
20	.8786	.8879	.9006	.9257	.9532	0.9904	1.0491
30	.8682	.8768	.8901	.9144	.9418	.9788	1.0376
40	.8574	.8657	.8796	.9032	.9307	.9675	1.0264
50	.8466	.8546	.8688	.8920	.9193	.9562	1.0153
60	.8357	.8436	.8582	.8810	.9078	.9448	1.0039
70	.8246	.8327	.8475	.8698	.8964	.9333	0.9923
	P_∞			P_2			
0	21.3	22.6	24.7	26.9	29.4	32.4	
10	22.4	23.8	25.3	27.5	30.0	33.1	35.6
20	22.8	24.2	25.7	28.1	30.6	33.7	35.9
30	23.1	24.5	26.2	28.7	31.3	34.3	36.7
40	23.7	25.5	26.6	29.2	31.9	35.0	37.3
50	24.2	26.1	27.2	29.8	32.5	35.5	37.9
60	24.8	26.8	27.6	30.4	33.0	36.1	38.6
70	25.5	27.7	28.2	31.0	33.6	36.7	39.4

Ether–Acetic Acid

	0	0 0339	0 0673	0 1039	0 1269	0 3549	0 5233	0 7198	1 000
0	4 746	4 817	4 869	4 966	5 015	5 489	5 793	6 28	
10	4 499	4 608	4 671	4 749	4 797	6 275	5 606	6 12	6 07
20	4 296	4 402	4 462	4 542	4 593	5 072	5 428	5 97	6 13
30	4 113	4 197	4 276	4 348	4 406	4 880	5 268	5 81	6 20
					d				
0	0.7370	0.7364	0.7532	0.7619	0.7669	0.8259	0.8731	0.9450	
10	.7254	.7276	.7414	.7504	.7556	.8146	.8628	.9342	1.0607
20	.7137	.7189	.7295	.7387	.7442	.8032	.8526	.9234	1.0491
30	.7021	.7102	.7176	.7271	.7328	.7918	.8424	.9126	1.0376
	P_∞				P_2				
0	64.0	57.3	57.3	45.6	44.9	41.0	39.5	38.6	
10	62.7	55.7	55.0	43.2	43.0	40.5	39.3	38.6	35.6
20	61.7	54.5	55.2	43.6	43.3	40.8	39.7	38.2	35.9
30	59.7	52.3	52.8	40.6	41.3	40.4	39.6	38.9	36.7

TABLE I (Concluded)

Benzene–Butyric Acid

Mole fr. C_3H_7COOH = t, °C.	0	0 0379	0 0640	0 0894	0 1875	0 4729	0 7183	1 000
10	2 315	2 301	2 333	2 342	2 388	2 542	2 705	2 932
40	2 253	2 266	2 280	2 290	2 340	2 519	2 715	3 001
70	2188	2203	2219	2231	2291	2500	2725	3.074
	d							
10	0.8896	0.8916	0.8933	0.8939	0.9026	0.9254	0.9435	0.9703
40	.8574	.8595	.8616	.8636	.8713	.8933	.9160	.9389
70	.8246	.8270	.8292	.8313	.8388	.8634	.8854	.9119
	P_∞	P_2						
10	31.4	31.2	32.4	33.0	33.5	34.7	34.6	35.6
40	33.1	33.7	34.5	34.3	34.8	36.3	36.6	37.5
70	33.9	34.5	35.8	35.6	36.6	37.9	38.4	39.5

of 3.6 ohms had to be inserted in series with the condenser in the opposite arm of the bridge to balance the small conductance of the liquid. At 85.1' the dielectric constant was 7.11 and the compensating resistance 41.5 ohms, and at 100.0° ϵ was 8.05 and the resistance 60.0 ohms. For the benzene solution containing a mole fraction 0.7912 of acetic acid, the resistance required at room temperature was negligible, but rose to 6.6 ohms at 90.6'. In the less concentrated solutions the conductance was negligibly small. In the ether solutions the conductances were small, as the temperature of measurement was not above 30°, but were detectable at concentrations of acid down to mole fraction 0.3549.

Discussion of Results

The acetic acid data in Table I do not agree precisely with the earlier unpublished values, but the small differences observed are no greater than might be expected in view of the difference in the material used and are insufficient to affect the conclusions to be drawn. When these earlier measurements were made upon acetic acid, the increase in the dielectric constant of the pure liquid with rising temperature was thought to be the first observed case of such a phenomenon, although it was known that the polarization of pure ethyl bromide increased with rising temperature. Since these first measurements were made, similar behavior has been observed for a number of secondary and tertiary octyl alcohols.[2] As the dielectric constants of the dilute benzene solutions decrease in the normal manner with rising temperature, there is an intermediate region of concentration within which the temperature coefficient of the dielectric constant is very small. Thus, the solution containing 0.6134 mole fraction of acetic acid shows a slight increase in ϵ with rising temperature up to 40° followed by an even more gradual decrease. The values of P_{12} which

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[2] Smyth and Stoops, THIS JOURNAL, 51,3330 (1929).

are not shown in Table I increase with temperature throughout the entire range of concentration, although the increase is very slight in the dilute solutions where the effect of the almost constant polarization, P_1, of the benzene predominates. As the polarization P_2 of the acetic acid in the dilute solutions is lower than that of benzene, the P_{12}–c_2 curves pass through a flat minimum in a region where there is little change of P_{12} with concentration.

The reason for this peculiar behavior is to be sought in the strong molecular association which is known to occur in acetic acid. Freezing point and partition coefficient measurements show that the apparent molecular weight of acetic acid in dilute solution in benzene is close to 120, the weight which it would have if polymerized into double molecules.[3] X-ray investigations indicate that the molecules of the higher fatty acids in the solid state are paired[4] end to end with their carboxyl groups in contact and a similar conclusion has recently been drawn for the liquid.[5] Such a pairing should bring the electric moments of the single molecules into opposition with resultant partial or complete cancellation of one another's effects. It is easy to picture the acetic acid in dilute solution in benzene as consisting largely of these double molecules possessing little or no electric moment. The concentration of single molecules is so low in the solutions here measured that extrapolation of the P_2 values to $c_2 = 0$ gives not the polarization of the molecules existing singly but rather their polarization when paired in the double molecules. Since these values of P_∞ increase with rising temperature, presumably because of increasing dissociation into single molecules, it is evident that they are not wholly free from the effect of the small number of single molecules present. It may be concluded, however, that the polarization of the molecules in this complex state is not far from 20. The molar refraction of acetic acid for the sodium D line is 13.0.[6] The difference between this and 20 is little, if any, larger than the value which the atomic polarization P_A might be expected to have. Consequently, the dipole contribution to the polarization, P_M, must be close to zero, if not actually zero, the electric moments of the single acetic acid molecules being practically canceled in the complex molecules. This conclusion is in agreement with results privately communicated some years ago by Dr. L. Ebert, who obtained 18.85 as the value of P_∞ for acetic acid in benzene and 19.4 for the molar polarization of the solid measured at 0° with a wave length of 5 meters. As there is no dipole contribution to the polarization of the solid measured under

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[3] Beckmann, *Z. physik. Chem.*, 22, 610 (1897); Herz and Fischer, *Ber.*, 38, 1138 (1905); Trautz and Moschel, *Z. anorg. allgem. Chem.*, 155, 13 (1926).

[4] Muller, *J. Chem. Soc.*, 123, 2043 (1923); Miiller and Shearer, *ibid.*, 123, 3156 (1923); Trillat, *Ann. phys.*, 6, 5 (1926).

[5] Morrow, *Phys. Rev.*, 31, 10 (1928).

[6] Landolt–Börnstein–Roth, "Tabellen," 5th ed.

these conditions, it is evident that P_∞ is made up of the electronic and atomic polarizations only, that is, $P_\infty = P_E + P_A$ and $P_M = 0$, which is equivalent to saying that the molecular complexes in the dilute benzene solutions possess no electric moment.

Apparently, when the concentration increases, these complexes, in spite of their lack of electric moment, affect one another sufficiently to cause increase of polarization. It seems possible that the higher dielectric constants of the more concentrated solutions may further the dissociation of the complexes into single molecules and so increase the polarization. The fact that the polarization increases with rising temperature would seem to support the attribution of the increase to the separation of single molecules rather than to the formation of a different type of complex. The absence of electric moment in the complexes in the dilute solutions and the closeness of the apparent molecular weight to that of a double molecule point to a polymerization to double molecules in which the carboxyl groups are in contact as indicated by the x-ray results. However, the mere assumption of the existence of single and double molecules without effect upon one another is inadequate to explain the observed phenomena. The freezing point measurements of Trautz and Moschel[3] give an apparent molecular weight of 117.5 for acetic acid when the mole fraction in the benzene solution is 0.0288, increasing to 124.9 when the mole fraction is 0.0650. This and similar results may indicate the formation of definite complexes containing more than two molecules, but it appears possible to explain the observed phenomena in terms of single and double molecules and strong intermolecular forces.

In the hope of reducing the intermolecular forces and the extent of the association, a solvent of higher dielectric constant than benzene was sought. Ether was adopted as being the only liquid of higher constant which, when dissolved in non-polar solvents, showed a polarization independent of concentration. Unfortunately, however, ether may form an addition compound with acetic acid and thus complicate the situation. The polarization of the acetic acid, P_2, calculated on the assumption that the polarization of the ether, P_1, is unaffected by the presence of the acid, shows a normal behavior, although the values for the dilute solutions contain errors larger than usual because of loss of ether by volatilization. The P_{12}–c_2 curve passes through a flat maximum in the region of high dilution where the apparent polarization of the acetic acid is higher than that of the ether. The value of P_M is calculated by subtracting from P_∞ the approximate value 20 found for $P_E + P_A$ and, from P_M, the electric moment 1.40×10^{-18} is obtained for the single acetic acid molecule. This value cannot be regarded as certain since it may be really the moment of an addition compound of acetic acid and ether, but there is some evidence in its favor.

In order to investigate the question of a definite equilibrium between single and double acetic acid molecules in ether solution, Mr. C. H. Lindsley has measured the distribution of acetic acid between water and ether at 25° over a range of concentration of 0.086 to 1.644 moles of acetic acid per liter of ether, a range within which lie the four most dilute solutions in Table I. The most constant value of the distribution coefficient was obtained when an equilibrium between single and double molecules was assumed. If a is the total number of moles per liter of acetic acid, all the acid being calculated as having molecular weight 60.04, and x is the concentration of single molecules, the equilibrium constant $K = x^2/(a-x)$. The mean value obtained for K was 2.7.

Since it has been shown that the double molecules have practically no moment and do not, therefore, contribute to the orientation polarization P_M and, since it has been assumed that the P_∞ obtained from the ether solutions is the polarization of the single molecules, the value of P_M observed at any concentration should be the orientation polarization for the single molecules $P_{M\infty}$ multiplied by the fraction of the acetic acid which is present as single molecules, that is, $P_M = (x/a)P_{M\infty}$. The values of P have been obtained by interpolation at 25° and those of P_M by subtracting from them $P_E + P_A = 20$. From the value $P_{M\infty} = 41$ thus obtained, the values of P_M have been calculated by means of K and the values of a and x calculated from it. The difference between the observed and calculated values of P_M is large at $c_2 = 0.1039$ and $c_2 = 0.1269$, but for the other solutions and the pure acid the average difference is only 1.9.

Since the value of K determined in the distribution measurements may be affected by the water with which the ether layer is saturated and since it may be different in the concentrated solutions and the pure acid from what it is in the dilute solutions, too much significance should not be attached to the agreement between the observed and calculated values of P_M. It may be said, however, that the entire behavior of acetic acid which has been described is consistent with the theory of its existence in single and double molecules, the force fields of which may affect one another and cause further abnormalities. As the moment of acetic acid might be expected to be not very different from that of methyl acetate, for which Williams[7] has found a value of 1.67×10^{-18}, the value 1.4×10^{-18} seems reasonable, but it must be borne in mind that there is a possibility that this is really the moment of an addition compound of acetic acid and ether.

The behavior of butyric acid is very similar to that of acetic. The dielectric constants of the pure liquid and the most concentrated solution increase with rising temperature. The dielectric constant is lowered

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[7] Williams, *Physik. Z.*, **29,** 174 (1928).

by the lengthened hydrocarbon chain, which reduces the number of dipoles in unit volume so that pure butyric acid behaves much like a benzene solution containing 0.6 to 0.7 mole fraction of acetic acid. The two methylene groups which differentiate butyric from acetic acid have a combined refraction for the sodium D line of 9.2, which is their contribution to P_E for the compound. This is very nearly the difference between the values of P_∞ for the two substances. The larger proportion of hydrocarbon in the butyric acid molecule lessens the rate of increase of the polarization with decrease in the concentration of benzene in the mixture so that pure butyric acid happens to have the same polarization as acetic.

The close resemblance of butyric acid to acetic is what would be expected from freezing point and partition coefficient measurements and the indication of double molecules by x-ray studies. The single butyric acid molecules must have approximately the same moment as those of acetic acid and form similar complexes in which the carboxyl groups are in contact with one another, canceling their moments.[8]

Summary

The dielectric constants and densities of solutions of acetic and butyric acids have been measured at different temperatures, and the data have been used to calculate the polarizations of the substances.

The dielectric constants of the pure acids behave abnormally in that they increase with rising temperature instead of decreasing.

The results are shown to be consistent with the theory of the existence of the acids in single and double molecules, the latter of which have little or no electric moment. It must be supposed, however, that the molecular force fields may affect one another and cause further abnormalities.

PRINCETON, NEW JERSEY

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[8] Since the submission of the manuscript of this paper for publication, Dr. *C.* T. Zahn has communicated to the authors a value 1.4 X 10^{-18} for the moment of acetic acid measured as vapor at high temperatures and low pressures where it must have existed as single molecules. This may be regarded as excellent confirmation of the value for what was thought to be the single acetic acid molecule in ether solution. Wolf, in a paper just published [*Physzk.* Z., 31, *227* (1930)], obtains a value of 0.74 X 10^{-18} for acetic acid from measurements in benzene solution at 22°, a value of 0.68 × 10^{-18} for butyric acid and 0.63 × 10^{-18} for both propionic and isovaleric acid. In calculating these results he used an estimated value of P_A equal to 15% of the molar refraction, which the evidence cited above shows to be much too small in the case of acetic acid. If $P - P_E$ in our results is used to calculate the moments of acetic and butyric acid, the values obtained are close to those calculated by Wolf. As it has been shown that $P - P_E$ consists mainly of the atomic polarization P_A for molecular complexes, the values calculated for moments from these differences and attributed to single molecules would seem to have little significance. These results also cast doubt upon the moment assigned to the carboxyl group in aromatic compounds from measurements upon the strongly associated benzoic acid in benzene solution [Williams, *Chem. Rev.*, 6, 589 (1929)].

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. X. THE ELECTRIC MOMENTS OF SIMPLE DERIVATIVES OF CYCLOHEXANE AND OF DIOXAN

BY JOHN WARREN WILLIAMS

RECEIVED JANUARY 16, 1930 PUBLISHED MAY 8, 1930

In the previous papers of this series there has been discussed the relation between electric moment data and the structure of benzene and a number of its derivatives. Another article[1] has been devoted to a study of the structure of derivatives of methane and ethane. It was thought that the extension of this type of study to cyclohexane and its derivatives would lead to a number of interesting conclusions, particularly because considerable information is now available concerning the structures of the mono- and di-substitution products of benzene.

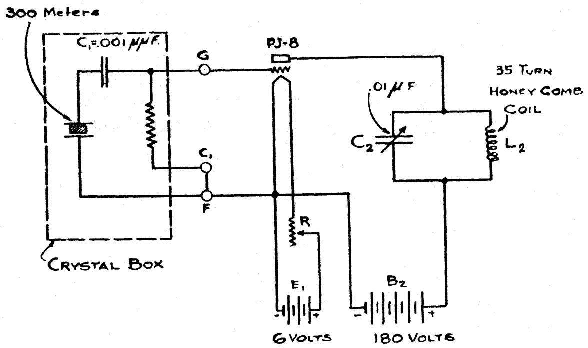

Fig. 1.—Crystal oscillator.

Experimental Method

The method of determining the electric moment of a solute molecule from dielectric constant and density data of a suitable binary mixture has been completely described in a number of places[2,3] and will not be repeated here. The measurement of the dielectric constants was made using an apparatus which was improved in several details over that previously described. A quartz crystal controlled circuit (frequency, 10^6 cycles) was used as the standard oscillator and a resistance-coupled three-tube detector and amplifier circuit replaced the transformer-coupled arrangement of the earlier investigations. The actual method of measurement of the dielectric constant of a solution was not changed from that which

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[1] Williams, *Z. physik. Chem.*, 138A, 75 (1928).

[2] (a) Williams and Krchma, THIS JOURNAL, 49, 1676 (1927); (b) Williams and Weissberger, *ibid.*, 50, 2332 (1928).

[3] Debye, "Polar Molecules," The Chemical Catalog Co., New York, 1929, et *al.*

has already been described. A diagram of the circuits used is given in Figs. 1 to 3.

Results

All chemicals used were carefully purified and their boilng points checked with those given in the "International Critical Tables." All dielectric constant and density measurements were made at 25°. The frequency 10^6 cycles was used for the dielectric constant determinations. The dielectric constant of benzene under these conditions was assumed to be 2.280.

The dielectric constant and density data for the various binary mixtures are given in Table I.

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA FOR MIXTURES

The symbols used have the following significance: f_1 is mole fraction of the solvent, in this case benzene; d_4^{25} is density of the solution; ϵ is dielectric constant of the solution; $P_{1,2}$ is molar polarization of the solution $= (\epsilon - 1)/(\epsilon + 2) \times [(f_1M_1 + f_2M_2)/d] = f_1P_1 + f_2P_2$; P_2 is molar polarization of the solute molecule.

f_1 (Benzene)	d_4^{25}	ϵ	$P_{1,2}$	P_2
		Cyclohexane		
100.00	0.8731	2.280	26.77	28
99.18	.8722	2.280	26.80	30
97.58	.8704	2 276	26 82	28
96 04	.8686	2.270	26.83	28
		Chlorocyclohexane		
100.00	0 8731	2.280	26.77	143
99.27	.8742	2.337	27.63	143
97.85	.8764	2.440	29.23	141
96.47	.8789	2.543	30.73	140
		Bromocyclohexane		
100.00	0.8731	2 280	26.77	150
98.89	.8798	2.363	28.10	149
97.48	.8884	2.489	29.96	153
96.79	.8965	2.567	30.94	156
		Cyclohexanone		
100.00	0.8731	2 280	26.77	202
99.15	.8741	2.385	28.29	205
97.40	.8761	2.605	31.27	200
		Methylcyclohexane		
100 00	0 8731	2.280	26.77	33
99 32	.8722	2 279	26.80	33
97 96	.8702	2.276	26.92	34
96.01	.8673	2.270	27.06	**34**
		Cyclohexanol[a]		
100 00	0.8735	2.276	26.66	105
99 64	.8737	2.292	26.93	103
99.12	.8740	2 318	27.32	101
98.25	.8745	2.357	27 93	99

[a] Data of Mr J. M. Fogelberg.

TABLE I (Concluded)

f_1 (Benzene)	d_4^{25}	ϵ	$P_{1,2}$	P_2
		1,4 Dioxan		
100.00	0.8731	2.280	26.77	26
97.90	.8762	2.283	26.79	28
96.00	.8793	2.290	26.84	29
94.10	.8824	2.300	26.96	30
		2-Methylcyclohexanol		
100.00	0.8731	2.280	26.77	113
98.44	.8744	2.360	28.06	110
97.20	.8757	2.437	29.26	114
95.95	.8770	2.504	30.29	114
		3-Methylcyclohexanol		
100.00	0.8731	2.280	26.77	108
98.50	.8743	2.356	27.99	108
97.23	.8755	2.414	28.91	106
95.95	.8768	2.496	30.19	110
		4-Methylcyclohexanol		
100.00	0.8731	2.280	26.77	106
98.42	.8743	2.353	27.96	103
97.21	.8755	2.416	29.01	107
95.89	.8768	2.487	30.07	107
		Cyclohexane carboxylic Acid		
100.00	0.8731	2.280	26.77	49
98.57	.8763	2.292	27.07	48
97.17	.8794	2.305	27.41	49
95.81	.8827	2.318	27.73	49

From the molar polarization of the solute molecules their electric moments have been calculated, making the assumption that that part of

TABLE II

ELECTRIC MOMENT DATA FOR SOLUTE MOLECULES

Molecule	P_2	P_2''	P_2'	$\mu \times 10^{18}$ e.s.u.
Cyclohexane	28	27.7	*ca* 0.3	0
Methylcyclohexane	33	32.7	*ca* 0.3	0
Chlorocyclohexane	143	33	110	2.3
Bromocyclohexane	150	36	114	2.3
Cyclohexanone	202	28	174	2.8
Cyclohexanol	105	30	75	1.9
1,4-Dioxan	26	22	4	0.4
2-Methylcyclohexanol	113	34	79	1.95
3-Methylcyclohexanol	108	34	74	1.9
4-Methylcyclohexanol	106	34	72	1.9
Cyclohexane carboxylic acid	49	33	16	0.9

In this table, P_2 is molar polarization of the solute molecule; P_2'' is polarization due to deformation of the molecule; P_2' is polarization due to orientation of the molecule; μ is electric moment of the molecule.

the total polarization which is due to the deformation of the molecule is given by the Lorentz–Lorenz formula, using the refractive index for the "D" line. The results of these calculations are believed to be correct to within **0.1** $\times$ 10^{-18} e. s. u., with the possible exception of dioxan, whose moment cannot be distinguished from zero by the method used. These data are presented in Table II.

Since the dielectric constants of but few of these derivatives of cyclohexane are to be found in the literature, measurements were made upon certain of the more common ones. The measurements were made in the manner described in the earlier papers of this series, using the apparatus which has just been described. It is evident that this method neglects the effect of any change in the absorption of energy in the liquid dielectric as the position of the rotor plates of the measuring condenser is changed. When substances like benzene and dilute solutions of polar molecules in benzene are studied, the absorption of energy is so low that corrections for this effect are not necessary. This is not the case, however, when appreciable and different amounts of energy are absorbed, and for precision measurements not only capacity changes but also resistance changes should be accounted for. For this reason the data, presented in Table III, are recorded to the nearest tenth of a unit only, since it was not possible to make the proper corrections. The results for the last four substances given are certainly the only ones which could be at all affected by this difficulty, and even in these cases the error introduced must be small.

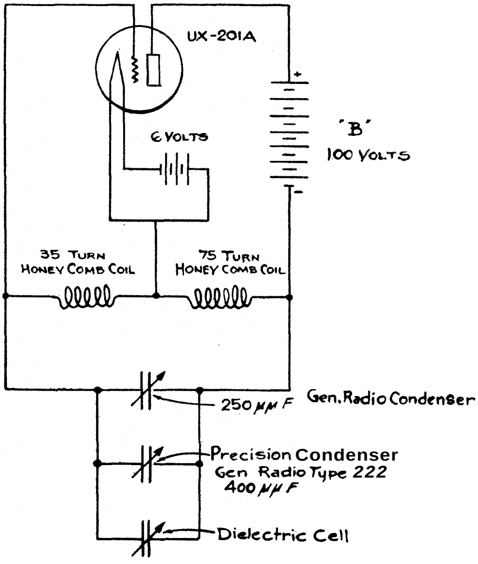

Fig. 2.—Variable oscillator.

TABLE III

DIELECTRIC CONSTANT DATA FOR CYCLOHEXANE AND ITS DERIVATIVES

Temperature, 25°. **Frequency, 10^6 cycles**

Molecule	Dielectric constant	Molecule	Dielectric constant
Cyclohexane	2.0	Bromocyclohexane	7.9
Methylcyclohexane	2.1	Cyclohexanol	15.0
1,4-Dioxan	2.2	Cyclohexanone	18.1
Chlorocyclohexane	7.6		

Discussion

There are now sufficient electric moment data for various mono-substitution products of cyclohexane, methane and benzene to be able to compare the effect produced by substituting a simple atom or group of atoms into these various parent substances. The data are collected in Table IV, in which those figures marked by the asterisk have been taken from other observers.[4]

TABLE IV

DATA FOR SUBSTITUTION PRODUCTS OF SIMPLE HYDROCARBONS

	Electric Moment X 10^{18}				Electric Moment X 10^{18}		
Atom or radical	For $C_6H_{11}\alpha$	For $C_6H_5\alpha$	Por $CH_3\alpha$	Atom or radical	For $C_6H_{11}\alpha$	For $C_6H_5\alpha$	For $CH_3\alpha$
H	0	0	0*	OH	1.9	1.65	1.65
Cl	2.3	1.5	2.0*	NO_2		3.9	3.1*
Br	2.3	1.5	1.9*	CH_3	0	0.4	0*
I		1.3	1.6	NH_2		1.5	1.2*
CN		3.85	3.4				

As one would expect, cyclohexane itself is a symmetrical molecule. When a CH_3 group is substituted into it, an electrically symmetrical molecule is again formed, since methylcyclohexane has a zero moment as well.

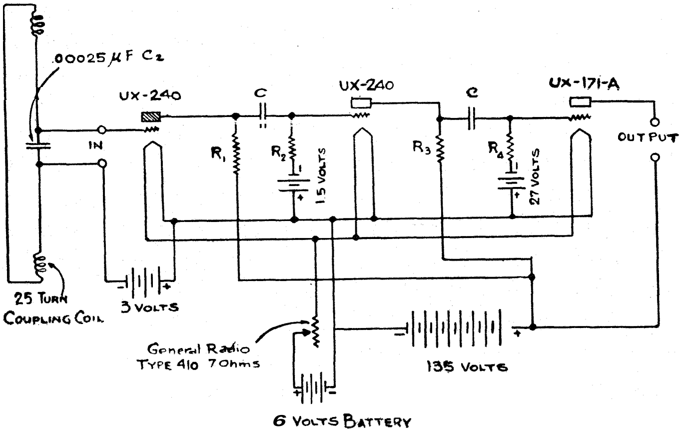

Fig. 3.—Detector-amplifier. CF $0.01\mu\mu$F.; R_2F 5 megohms; $R_1 = R_3$F 0.25 megohms; R_4F 5 megohms.

Thus cyclohexane behaves like methane and not like benzene on the substitution of a CH_3 group. Toluene is a slightly polar substance. Furthermore, Raman spectra for benzene and for toluene indicate distinct differences in energy levels which are not found in methane hydrocarbons and presumably will not be found in cyclohexane hydrocarbons,[5] so that

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[4] Debye, "Polare Molekuln," Table of Dipole Moments, Hirzel, Leipzig, 1929.

[5] Kohlrausch and Dadieu, *Physik. Z.*, 30, 385 (1929); Reynolds and Williams, THIS JOURNAL, article submitted March, 1930.

these two types of study lead to similar conclusions involving two different carbon to carbon linkages.

The electric moments for chlorocyclohexane and bromocyclohexane are practically identical. This might have been predicted since the corresponding derivatives of methane and of benzene, respectively, also have like values. The moment produced in the cyclohexane derivatives is distinctly higher than that of the other compounds in question. Also, the substitution of an hydroxyl group in cyclohexane produces a more polar molecule than the substitution of the same group into benzene or methane. This appears to be a matter of internal compensation of charges about which little is known in a quantitative way at present.

The data for cyclohexane carboxylic acid are to be compared with those previously reported[6] for benzoic acid. In each case the molar polarization of the solute molecule is constant over a considerable range of concentration. This is a surprising result, because, at least for benzoic acid and presumably for cyclohexane carboxylic acid as well, the molecular weight of the solute in benzene solution increases as its concentration is increased. In other words, the degree of association of the solute is increasing with increasing concentration and, therefore, according to the explanation given this phenomenon by Debye,[3] the molar polarization of the dissolved molecule should either increase or decrease, the latter being more probable. The same reservation must be made for the value of the electric moment reported for cyclohexane carboxylic acid as was made for benzoic acid, namely, that it is difficult to state exactly what the effect of this association will be upon the result. The moment reported is to be considered of the right order of magnitude only. It is possible that measurements over a range of temperature would be of material assistance in assigning more definite values for the electric moments of these two compounds.

The data for the methylcyclohexanols are of interest in connection with the data for the cresols.[7] For the latter it will be recalled that each had a smaller moment than phenol, and that the moments for the meta and para compounds were practically identical. The electric moments of the three methylcyclohexanols are in every case of identical magnitude with that of cyclohexanol itself and are all three practically identical. The fact that all four molecules have nearly identical moments is not surprising. The moment is characteristic of the OH group alone and is quite independent of the presence of the CH_3 group. This result was to have been expected from the zero moment found for methylcyclohexane. It is also true that these substances, bought under the names used in the tables from the Eastman Kodak Co., may be mixtures of isomers; in that event the electric moments reported are average values for equilibrium

[6] Williams and Allgeier, THIS JOURNAL, 49, 2416 (1927).

[7] Williams, *Physik. Z.*, 29, 683 (1928).

mixtures. Because of the possibility of isomerism it is evident that any extension of dipole moment studies to disubstituted cyclohexanes will be considerably more difficult and involved than the corresponding study of benzene derivatives has been. Nevertheless it should be an interesting problem.

There are included in Tables I and II the results of measurements for solutions of 1,4-dioxan in benzene. Dioxan is found to have an electric moment which can differ but slightly, if at all, from zero ($\mu = 0.4 \times 10^{-18}$ e. s. u.) in spite of the fact that there must be two very active parts in the molecule. This interesting chemical, though not classed as a derivative of cyclohexane, has a ring structure and has certain properties in common with cyclohexanol and cyclohexanone. Since it is such an unusual solvent and at the same time a molecule of extremely low polarity, it was thought that it might serve as as uitable solvent for the determination of the electric moments of substances insoluble in the usual nonpolar solvents. This idea will form the basis of the next article of this series.

Summary

1. Dielectric constant and density data at 25° have been obtained for dilute benzene solutions of cyclohexane, chlorocyclohexane, bromocyclohexane, cyclohexanone, methylcyclohexane, cyclohexanol, 1,4-dioxan, 2-methylcyclohexanol, 3-methylcyclohexanol, 4-methylcyclohexanol and cyclohexane carboxylic acid. The electric moments of the solute molecules have been calculated.

2. Certain improvements, shown only by diagram, have been made in the apparatus used to measure the dielectric constants.

3. The electric moment data for the various derivatives of cyclohexane have been compared with those for the corresponding derivatives of benzene and methane.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. XI. THE USE OF DIOXAN AS A SOLVENT FOR ELECTRIC MOMENT STUDIES

BY JOHN WARREN WILLIAMS

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There are at present two methods by which the electric moment of a molecule may be determined, as follows: (1) from the temperature coefficient of the dielectric constant of a gas or vapor;[1] (2) from dielectric constant and density data for suitable binary mixtures.

The previous articles of this series have utilized the second of these methods, for while it is perhaps not as sound theoretically as the first one, it is easier from an experimental viewpoint and does give a result which is in good (though not exact) agreement with that of the first method. The latter statement has now been amply verified. It has been the purpose of these articles to show the application of a new physical method to the study of the structure of molecules—an important chemical problem.

Both methods have difficulties inherent in them. For example, the electric moments of a number of organic molecules may never be determined by the first method because these substances are unstable in the vapor state. The second method is not as yet a general one because for it there are required "suitable" binary mixtures. A suitable binary mixture is defined as one in which one of the components, the solvent, is non-polar, that is, its electric moment is zero. Benzene, carbon tetrachloride, carbon bisulfide and hexane are liquids having no moment and considered to be suitable solvents for electric moment determinations of this sort. Unless other solvents can be found the second method will then be applicable only to those substances which can be dissolved in these solvents to the extent of something like 1%, using the best apparatus now available for the dielectric constant and density determinations. Measurements have been made for substances having lower solubilities, but the results cannot be considered to be entirely dependable. Thus the electric moment of the water molecule has been calculated from dielectric constant and density data for a saturated solution of water in benzene,[2] but it can only be claimed that the result is of the right order of magnitude.

Several recent articles have discussed the solvent properties of 1,4-dioxan.[3,4] It is found to be an excellent solvent for a large number of

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[1] Dielectric constant measurements on gases and vapors at a single temperature have also been utilized for this purpose.

[2] Williams, *Physik.* Z., 29, 204 (1928).

[3] Anschutz and Broeker, *Ber.*, **59B,** 2844 (1926).

[4] Reid and Hofmann, Ind. Eng. *Chem.*, 21, 695 (1929)

substances, inorganic as well as organic. Its electric moment, reported in the previous article of this series,[5] is not greater than $\mu = 0.4 \times 10^{-18}$ e. s. u. This value is so small that it is indistinguishable from zero by the method used; therefore it seemed possible that dioxan might act as a non-polar solvent, in spite of the fact that it is a molecule containing two very active groups. Dielectric constant and density data at 25° were obtained for dilute solutions of chlorobenzene, water, chlorocyclohexane and *o*-diethyl phthalate in 1,4-dioxan, and the molar polarizations of the respective solute molecules were calculated, making the assumption that the polarization due to the solvent dioxan was always exactly proportional to its mole fraction in the solution. The electric moments were calculated from the molar polarizations in the usual manner. These four substances were chosen at random to represent different types of molecules. In the interest of a saving of space the dielectric constant and density data for the four mixtures have not been included. The results of the calculations of the electric moments of the solute molecules are presented in Table I. The symbols used have been defined completely in the previous article.[5]

TABLE I

ELECTRIC MOMENT DATA FOR SOLUTE MOLECULES

Molecule	P_2	P_2''	P_2'	$\mu \times 10^{18}$ e s u.
Chlorobenzene	80	31	49	1.5
Water	82	4	78	1.9
Chlorocyclohexane	146	33	113	2.3
o-Diethyl phthalate	226	60	166	2.8

Electric moment data for chlorobenzene, water and chlorocyclohexane are available in the literature. The electric moment of o-diethyl phthalate was determined from dielectric constant and density data (Table II) for this substance in dilute benzene solution.

TABLE II

DIELECTRIC CONSTANT AND DENSITY DATA FOR BINARY MIXTURE BENZENE–*o*-DIETHYL PHTHALATE

f_1 (Benzene)	•	d_4^{25}	$P_{1,2}$	P_2
100.00	2.280	0.8731	26.77	206
99.64	2.316	.8756	27.37	202
99.29	2.360	.8782	28.10	209

Finally, there is given in Table III the comparison of the polarization and electric moment data for the four solute molecules obtained from benzene solution and from dioxan solution.

The only conclusion to be drawn from this table is that dioxan is just as good a solvent as benzene for determinations of the electric moments of these particular molecules. For chlorobenzene and chlorocyclohexane

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[5] Williams, THIS JOURNAL, 52, 1831 (1930).

TABLE III

COMPARISON OF DATA USING DIOXAN AND BENZENE AS SOLVENTS

Molecule	Solvent	P_2	P_2'	$\mu \times 10^{18}$
1 Chlorobenzene	C_6H_6	82	51	1.5
	$C_4H_8O_2$	80	49	1.5
2 Water	C_6H_6	64	60	1.7[2]
	$C_4H_8O_2$	82	78	1.9

Electric moment of water, calculated from temperature coefficient of dielectric constant of water vapor = 1.85–1.87.[6]

Molecule	Solvent	P_2	P_2'	$\mu \times 10^{18}$
3 Chlorocyclohexane	C_6H_6	143	110	2.3
	$C_4H_8O_2$	146	113	2.3
4 o-Diethyl phthalate	C_6H_6	205	145	2.7
	$C_4H_8O_2$	226	166	2.8

the results are identical, within the limits of experimental error. Dioxan would appear to be the more desirable solvent for the determination of the electric moment of the water molecule, since the value obtained using it, $\mu = 1.9 \times 10^{-18}$ e. s. u., is identical, to two significant figures, with the commonly accepted value obtained from the temperature coefficient of the dielectric constant of the vapor. The molar polarization value for o-diethyl phthalate obtained from the dioxan solution is somewhat higher than the corresponding value obtained from the measurements in benzene solution. Indeed, there is good reason to believe that in a number of cases the resulting molar polarization obtained in dioxan solution will be somewhat higher than they should be. Since dioxan contains two very active groups in the molecule, one might expect segregation and orientation effects upon solute molecules which happen to be within a certain distance of these more active centers.[7] These orientation effects would result in an additional polarization contributing to the total polarization. In this case the assumption could hardly be made that the polarization due to the dioxan (as solvent) is always exactly proportional to its mole fraction in solution.

Furthermore, in spite of the fact that it is a stable substance it does form addition compounds with both organic and inorganic substances in solution. It is evident in the event of a compound formation between solvent and solute that the dielectric constant and density measurements would be of little significance.

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[6] Jona, *Physik. Z.*, 20, 14 (1919); Sanger, in Debye, "Leipzig Lectures," S. Hirzel, Leipzig, 1929.

[7] These segregation and orientation effects are important not only in connection with measurements of molar polarization but also in connection with numerous chemical phenomena. For example, they will undoubtedly have to be considered in the study of solubility relationships and in the study of reactions in solution. These effects, now the subject of further investigation by us, have been defined by Langmuir [*Chem. Rev.*, 6, 451 (1929)].

It is not claimed as a result of this table that dioxan is a suitable solvent for the determination of the electric moment of any dissolved molecule in the same sense that either benzene or carbon tetrachloride is, However, it does appear possible that dioxan may be used to determine at least the correct order of magnitude of the electric moment of molecules which are difficultly soluble in the recogaized non-polar solvents. For example, if the electric moment of the water molecule could not have been determined by studying the temperature coefficient of the dielectric constant of its vapor, the value obtained from the dioxan solution would have indicated that the value obtained from the single solution of water in benzene could not be greatly in error. Indeed, it would be desirable to make comparison measurements in some solvent like dioxan in every case where the solute molecules are so difficultly soluble that measurements for only one (very dilute) solution can be made.

Another use of dioxan suggests itself. In a practical way it should be a suitable solvent in which to study the electrical properties of cellulose derivatives, gums, resins and other more complicated organic compounds, the idea being that certain information concerning the sizes and shapes of the various substances could be made available.

Summary

1. Dielectric constant and density data have been obtained for dioxan solutions of chlorobenzene, water, chlorocyclohexane and o-diethyl phthalate and for benzene solutions of o-diethyl phthalate.

2. The electric moments of the solute molecules calculated from the data in dioxan solution are compared with those obtained using the usual non-polar solvents, and found to be in good agreement.

3. It is suggested that while dioxan is probably not a suitable solvent for the determination of the electric moment of any dissolved molecule, it does offer interesting and important possibilities in cases where the usual solvents cannot be used.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

THE SOLUBILITY OF GOLD IN MERCURY. II

BY ARTHUR A. SUNIER AND CHESTER M. WHITE

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Although several investigators[1] have worked on the system gold-mercury, the majority of the results have been confined to temperatures above 100°, and strangely enough the few values between 0 and 80° disagree remarkably with each other—differences of several hundred per cent. being common in this temperature range. Quite recently a rather precise piece of work was published by Sunier and Gramkee on the solubility of gold in mercury from 80 to 200°, using the tube of Sunier and Hess[2] slightly modified. It was thought advisable, therefore, to continue these measurements with the apparatus just mentioned. This paper will present results on the solubility of gold in mercury from 7 to 80°. In spite of the low apparent solubility (0.1 to 0.5%) in this temperature range, the precision of measurement is considered to be excellent, the average deviation from the mean for all the determinations being about 5 parts per thousand, which corresponds on the average to about 0.001 atomic %.

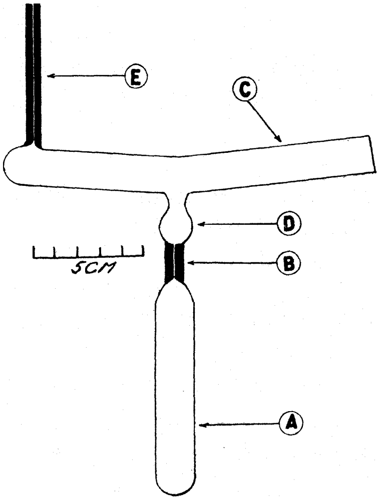

Fig. 1.—Solubility tube.

Materials.—Mercury was covered with a considerable amount of dilute nitric acid and air was aspirated through the mercury for a week; it was then distilled several times in an all-glass apparatus under diminished pressure, according to the method of Hulett and Minchin.[3] Samples of this mercury yielded no weighable residues when slowly evaporated at 270° in a current of air. The gold was used in the form of foil which had been rolled from a bar of gold said to contain less than 0.05% impurity.

Apparatus.—The solubility tube, Fig. 1, a modification of the one used by Sunier and Gramkee, was made of pyrex glass and consisted of a sample tube, A, capillary filter, B, a tube for preparing amalgams, C, the cup, D, and the capillary, E, both of which were used in filtering the amalgams. The dimensions of the tube were increased at lower temperatures to accommodate larger volumes of mercury.

The shaking and sampling apparatus differed considerably from that used in the

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[1] Parravano, *Gazz. chim. ital.*, 48, II, 123 (1918); Braley and Schneider, THIS JOURNAL, 43, 740 (1921); Britton and McBain, *ibid.*, 48, 593 (1926); Sunier and Gramkee, *ibid.*, 51, 1703 (1929); Kasanzeff, *Ber.*, 11, 1255 (1878), determined the solubility of gold in mercury at 0, 20 and 100°.

[2] Sunier and Hess, THIS JOURNAL, 50, 662 (1928).

[3] Hulett and Minchin, *Phys. Rev.*, 21, 288 (1905).

first research, and since it proved so satisfactory it will now be briefly described. The apparatus was designed with a view to making it possible to handle the low and high sides independently or simultaneously at will.[4] Figures 2 and 3 give front and side views, respectively, of the apparatus; these views correspond to the sampling and rotating positions, respectively. The apparatus is built in two units which are nearly identical; each unit is capable of carrying four solubility tubes; only one tube, however, is shown in Fig. 2 in order not to complicate the figure.

A large round piece of brass rod, R, was drilled to slip over the axle, G, and was fitted with suitable clamps to hold the tubes firmly in position. A cotter pin through G served to hold R in position. The axle G was supported by the square brass rod H, which in turn, was securely damped to rigid supports (not shown in Figs. 2 and 3). A smaller rod M was fixed to R in a manner indicated, and was connected by the long rod J to the eccentric; thus a motion could be given the tubes as indicated by the full and dotted lines in Fig. 3. The rods JJ could easily be detached from the eccentric and were used in rotating the tubes through 180° at the time of filtering.

The two units differ only in the rods H and I. Rod H was never removed from the bath and was always used to support the four tubes that corresponded to the high side. When the other unit (constituting the low side) was to be inserted in the bath, the peg N on the rod I was put in the hole in cated on the rod H; then the movable rod Q was pushed to the left until the two rods I and H were securely fastened together. It should be apparent then that each set of tubes could be inserted in the bath, rotated and sampled independently of the other set.

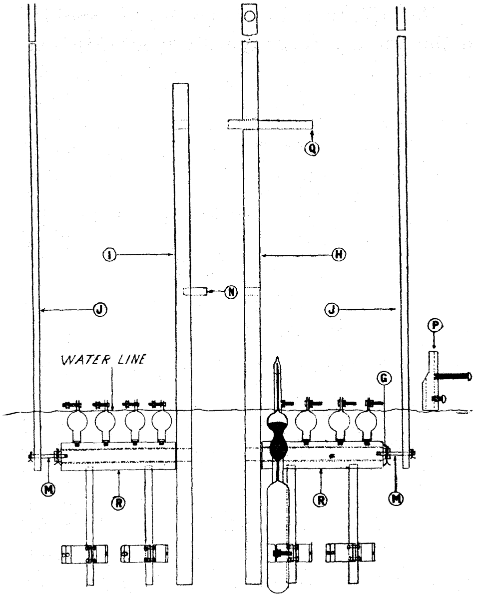

Fig. 2.—Shaking and sampling apparatus.

The tubes were immersed in a thermostat, which was very heavily lagged and contained 334 liters of water.[6] The top of the thermostat was partly covered in all the runs except in those at 70 and 80" where it was completely enclosed to prevent excessive evaporation of the water. Two or three centimeters of the sampling tubes projected above the water level in all the runs except in series I, where the entire tube was submerged. A revolving shaft, loaded with forty oil sample bottles, produced the necessary agitation within the bath. The bath could be heated by steam and by six 500-watt heaters; it could be cooled to temperatures below that of the room by running cold water through a special cooling coil, or by adding finely mashed ice directly to the water; this latter procedure was resorted to in run F (7°). In some of the runs a thermoregulator

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[4] Mr. Law G. Weiner, working in the laboratory, first applied this idea (but his apparatus was necessarily quite different) in determining the solubility of gold in mercury at high temperatures.

[5] It is hoped to publish in another place further details concerning this type of thermostat, which has proved very satisfactory during the eight years of its use.

was used; in others hand regulation was resorted to. In either case variations of temperature as large as 0.1° occurred very rarely and only for a very short time. A Beckmann thermometer inserted in the bath was read at frequent intervals and indicated that the average temperature variation was about ±0.02°.

The temperatures were read from two mercury thermometers (graduated in tenths of a degree) which were compared with thermometers recently standardized by the Bureau of Standards. Temperatures are recorded to the nearest 0.02°, which was readable with ease. .

Experimental Procedure

A certain volume of mercury (depending on the temperature of the run) was charged in the tube D (Fig. 1) with about 100% excess of gold, using Britton and McBain's data as a guide, with the solubility tube in a horizontal position. A rubber tube and pinch clamp on the capillary E prevented the mercury from running out. After sealing off at D, the mixture was transferred to the opposite end of the tube and the capillary E was attached to a Cenco Hyvac pump. When the tube was thoroughly evacuated and outgassed, the capillary was sealed off and file marked.

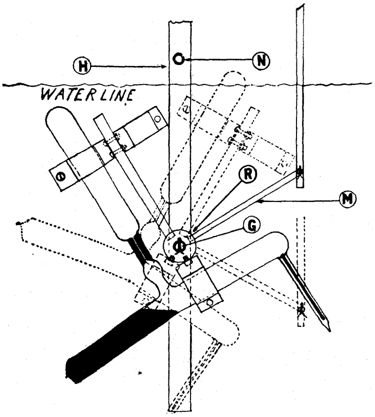

Fig. 3.—Shaking apparatus (side view).

To determine the solubility at a certain temperature saturation was (with two exceptions, Runs E and F) attained from both the high and the low sides. A total of eight tubes was made up and four were placed in each rack. One set was introduced and rotated for two and one-half to three hours when the bath was about 5° above the solubility temperature. This constituted the high side of the run. The temperature was then allowed to drop to the desired point when the remaining four tubes were inserted; all eight tubes were then shaken for three to four hours (in one case six hours) at constant temperature. By running the high and low side determinations together, considerable time was saved.

When it was time to sample, the connecting bars JJ were slipped from the eccentric and used as handles to rotate the tubes through 180°. Water was allowed to run out until the entire length of capillary E projected above the water level. A piece of brass rod (P), drilled to fit the capillary, was provided with two screws, one of which (lower) held the breaker fast while the second produced the necessary pressure above the file mark, which would break the capillary.[6] After filtration, the tubes were taken from the bath. The sampling tubes were cut off and their contents transferred to weighed crucibles. Some of the empty used tubes were cleaned thoroughly and repaired and were thus used for more than one determination.

To analyze the amalgams, the evaporation method was used which Sunier and Gramkee have shown to yield results 0.2% high if proper precautions are taken. Since it was known that hydrogen would not be available at all times during the course of this research, air was used in place of hydrogen. Carefully performed experiments seem to indicate that the results are identical in both cases. It should be noted that occasionally a small amount of a red powder was visible on the sides of some of the capsules when

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[6] This improved breaker was designed and used by Mr. Law G. Weiner in another research.

held below 300°. On heating to about 550° this powder always disappeared, thus indicating that some mercuric oxide was formed at the lower temperatures. These observations appear to be in accord with the free energy changes for mercuric oxide given by Lewis and Randall,? who made use of data determined by Taylor and Hulett.[8] The capsules were placed on iron supports in a large pyrex tube, which was electrically heated. Air was passed through the tube, which was heated to 270° until no mercury was visible. Since the danger of bumping was lessened with these dilute amalgams, a higher evaporation temperature was employed. After heating the gold residues for ten to twelve hours at 450 to 550°, they were weighed and then reheated for three more hours when they were again weighed. If their weights differed by more than two-tenths of a milligram, the residues were further heated until this degree of constancy was obtained.

To test the entire experimental arrangement, six tubes were made up with weighed amounts of gold and mercury,[9] and were carried through the entire procedure. The results are given in Table I. The average differences in the values in columns four and five are seen to be a little less than 2 parts per thousand, which would appear to be very good, considering the small amount of gold weighed; furthermore, the averages of these two columns differ by less than one part per thousand.

TABLE I

ANALYSIS OF AMALGAMS OF KNOWN CONCENTRATION

No.	Gold taken, g.	Mercury taken, g.	Atomic % taken	Atomic % found	Diff., p. p. t.
1G	0.1957	67.357	0.2959	0.2958	0.4
2G	.1945	68.426	.2898	.2901	1.0
3G	.1740	67.517	.2628	.2631	1.0
4G	.1881	67.910	.2824	.2829	1.7
5G	.1961	68.433	.2921	.2906	5.0
6G	.1998	68.096	.2990	.2985	1.7
		Average	.2870	.2868	1.8

Experimental Results

In Table II will be found complete data for two temperatures, while Table III contains a summary of all the data obtained. In Table IV will be found the solubility at rounded temperatures, taken from the log N vs. $1/T$ plot.

TABLE II

SOLUBILITY OF GOLD IN MERCURY. COMPLETE DATA FOR TWO TEMPERATURES

No.	Temp., °C.	Approx. wt of Au at start	Wt. of gold, g.	Wt. of amalgams, g.	Atomic % sol.
1E	High side	0 4	0 1176	92 240	0 1296
2E	at	.4	.1402	117.456	.1280
3E	20.00	.4	.0942	72.741	.1299
4E	Low side	.4	.1478	115.573	.1307

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[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, 1923, pp. 483, 484.

[8] Taylor and Hulett, J. Phys. *Chem.*, **17,** 565 (1913).

[9] In making up the knowns, a small amount of mercury was probably vaporized during the outgassing procedure; this constituted a source of error which was not present in the regular procedure.

TABLE II *(Concluded)*

No.	Temp., °C.	Approx. wt. of Au at start	Wt. of gold, g.	Wt. of amalgams, g.	Atomic % sol.
5E	(see text)	0.4	0.1391	111.089	0.1279
6E	at	.4	.1467	117.360	.1276
7E	20.00	.4	.1304	103.300	.1292
				Average	.1290
1I	High side	1.0	0.3080	67.269	0.4680
21	at	1.0	.3047	66.955	.4652
31	80.40	1.0	.3084	67.525	.4669
51		1.0	.3175	70.010	.4636
61	Low side	1.0	.3213	70.783	.4626
71	at	1.0	.3144	69.793	.4605
81	80.40	1.0	.3063	67.141	.4663
				Average	.4647

TABLE III

SOLUBILITY OF GOLD IN MERCURY (SUMMARY OF EXPERIMENTAL DATA)

Series no.	No. of detns.	Temp., °C.	Atomic % sol.	Av. dev. (from the mean), p.p.t.
F	5	6.96	0.1006	8.2
E	7	20.00	.1290	7.7
D	6	29.68	.1638	4.7
C	6	39.98	.2045	5.4
B	4	49.50	.2461	4.1
A	6	60.32	.3152	5.2
H	7	70.36	.3753[a]	3.1
I	7	80.40	.4647[a]	4.3

[a] Several years ago Mr. C. B. Hess, working in this Laboratory, made some determinations of the solubility of gold in mercury; his results, which were distinctly preliminary in character, are tabulated here

No. of detns.	Temp., °C.	Av. atomic % sol.
3	69.2	0.375
3	83.8	.498

The method of analysis was nearly identical with that used by Fitzsimmons; whose method was described in the first paper of this series. The temperatures were read from uncalibrated thermometers, hence it did not seem proper to include these results in Table II. It should be pointed out that the agreement in the two series of determinations is all that could be desired.

TABLE IV

SOLUBILITY OF GOLD IN MERCURY AT ROUNDED TEMPERATURES (FROM LOG N *vs.* $1/T$ PLOT)

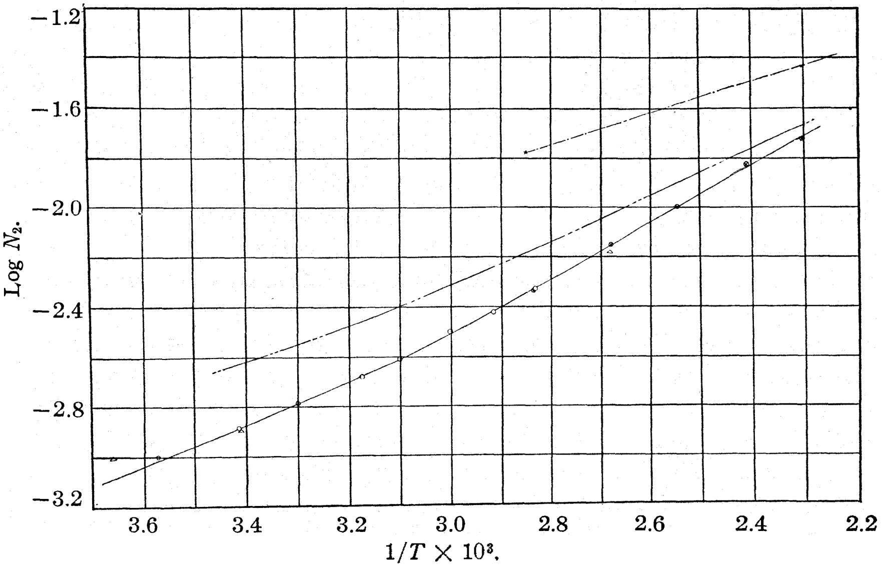
Temp., °C.	0	10	20	30	40
Atomic % sol.	(0.0813)[a]	0.1038	0.1306	0.1629	0.2014
Temp., °C.	50	60	70	80	
Atomic % sol.	0.2489	0.3076	0.3767	0.4614	

[a] Extrapolated value.

Of the fifty-six determinations, eight have been omitted, because the deviation of each was greater than four times the average deviation from the mean for that temperature. All solubilities are given in atomic per cent. (atoms of gold per 100 total atoms). Atomic weights as follows were used in the calculations: Au = 197.2, Hg = 200.61.

Discussion of Results

From the log N vs. $1/T$ plot (Fig. 4) it is seen that the present results are considerably lower than most of the previously published values. The present work appears to be in excellent agreement with the data presented by Sunier and Gramkee, the respective values reported at 80° being 0.4614% and 0.459%. The determination of Kasanzeff at 100° is in good agreement with the work of Sunier and Gramkee. Kasanzeff's three determinations were made about fifty years ago by an apparently crude method (the whole article of this author is really only an abstract, three paragraphs long). Britton and McBain's values are high at lower temperatures, but approach the authors' values as the temperature is raised.[10]



△, Kasanzeff; — - —, Parravano; — - - —, Britton and McBain; -⊗-, Sunier and Gramkee; -⊙-, Authors.

Fig. 4.—Solubility of gold in mercury.

Qualitative proof of the solubility at 25° was obtained from some preliminary experiments. Weighed quantities of gold and mercury, which corresponded to an average value of Britton and McBain's data at 18°,

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[10] From unpublished work of Mr. Law G. Weiner, working in this Laboratory, it appears that these investigators are low at about 230". Incidentally, he does not find the maximum which they report.

were sealed in pyrex test-tubes and rotated for four hours at constant temperature (25°). At the end of this period, the gold foil was plainly visible, thus indicating that Britton and McBain's data are high at these lower temperatures. Braley and Schneider's results, which differ so radically from the present work, could not be conveniently plotted. It would seem that some serious error had been made in obtaining their data, which indicate a solubility of 15 atomic per cent. at 20°. Parravano has only two determinations in the temperature range plotted in Fig, 4; the results obtained in these determinations would appear to be much too high. It is well known that fusion curve methods often give high results if proper precautions are not taken.

The present results, however, are higher than the values which one gets from the equation of Sunier and Gramkee, $\log_{10} N = (-1167.4/T) + 0.996$, which was valid from 80 to 160°; consequently, when both sets of data are plotted, the resulting curve is not a straight line, nor was it possible to obtain a simple equation for this curve. Of the three possibilities, (1) solid phase may not be the one indicated, (2) an actual transition may take place at the temperature where the break occurs, (3) the latent heat of fusion of the solid phase is a function of the temperature, the last one seems to offer the best explanation; it should be mentioned, however, that the nature and composition of the solid phase in equilibrium with the solution has not been determined by any of the above-mentioned, investigators,[11] each (with one exception) suggesting a different compound. It would seem that evidence has been obtained in another research, unpublished but mentioned earlier, which tends to prove that the maximum in the solubility curve reported by Britton and McBain is quite likely in error, and thus the formula of the compound suggested by these workers is in error. Very recently Pabst[12] has published the results of an x-ray investigation of this system. Solid solutions appear to be present in the concentration range 0 to 15% mercury. Work in the range considered in this paper has apparently not been completed, but the author makes the general statement that there are several other phases of undetermined structure in the mercury-rich end of the diagram. It is to be hoped that these investigations may be continued and that other methods may be used in attempting to check the results that may be obtained.

At this point it might be well to mention the few sources of error in the apparatus and method. In the first paper attention was called to the error that might arise if the bore of capillary E was too large. In runs

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[11] Since this was written it has been possible to look into the recent publication of I. N. Plaskin [*J. Russ. Phys.-Chem. Soc.*, **61**, 521 (1929)] who declares that the compound $AuHg_2$ is stable under the conditions existing in the experiments recorded in the present paper. It is hoped to discuss Plaskin's work more fully in the near future.

[12] Pabst, *Z. physik. Chem.*, **3B**, 443 (1929).

A to F, the only available capillary had such a diameter that a 2-cm. length contained about 0.6 g. of mercury; but since the tubes were made up twelve hours or more before being used (and the gold was always in contact with the mercury during this interval) the mercury may well have become saturated with gold at room temperature, which was 25° or a little higher. It should be quite evident that in the runs at 20 and 30° the concentration of gold in the mercury in the capillary was nearly the same as in the main body of the amalgam; the same was nearly true of the runs at 7 and 40°. In the runs at 50 and 60° the concentration of gold in the mercury in the capillary was about half (see Tables 111 or IV) that in the main body of the amalgam; thus the results at 50 and 60° may, at the *most*, be low by $(0.6/2/80)100 = 0.4\%$. The capillary available for the runs at 70 and 80° had a bore sufficiently fine so that no appreciable error arose from this cause.

In a few of the runs the folded strips of gold foil caught occasionally on the sides of the tubes and were not transferred with the amalgam every time; therefore, an excess of gold was not always in contact with the amalgams for the entire shaking period. Since the authors feel that a better technique was developed in the later runs, the first determination was not weighed as heavily as the succeeding ones. (The series numbers in Table III indicate the order in which the runs were made—A first, B next, etc.)

Run F (7") gave high results probably because the sampling tube was not long enough to contain the large volume of amalgam; consequently, some of it remained in the filter cup with the excess gold, after the tubes were taken from the bath. Possibly some of this more concentrated amalgam might have fallen into the filtered portion while the sampling tube was being broken. Three determinations were omitted from the average in this determination because their deviation was more than four times the average.

Throughout the temperature range 7 to 80°, the temperature coefficient of solubility was such that one-tenth degree corresponded to about 2 parts per thousand change in the solubility; since the temperature of the bath was held to ±0.02°, it would appear that no appreciable error arose from this cause.

In conclusion then it is felt that since the method of analysis of very dilute amalgams (described above) has proved so reliable and since the precision of measurement in the various determinations is so good, the values presented in Table IV appear to be considerably more accurate than those published heretofore.

Bearing of Data on **the** Metallurgy of Gold.—The amalgamation process for the mining of gold consists essentially of treating the crushed ore with mercury, which amalgamates with the gold and leaves impurities on the surface of the mercury. Later the solid amalgam which settles out, is distilled to remove the mercury from the metal.

The explanations which have been put forth to account for the extraction of gold by mercury are rather indefinite and somewhat confusing. Mellor[13] states, "The gold is miscible with mercury in all proportions. . . ." Evans[14] says, "Gold is soluble in mercury. . . .," and farther on he writes, "It should be pointed out that the actual catching of the gold grains by amalgamated plates is a process of surface adhesion; the dissolution of the adhering gold in the mercury to form an amalgam occurs slowly after the grains have been caught." From these quotations, it is seen that solubility is believed to play an important part in the formation of the amalgam. From the present results, however, the solubility appears to be 0.1306 atomic per cent. at 20°. A simple calculation shows that 100 pounds of mercury would only dissolve 2 ounces of gold (the amount found in a ton of some ores) which is far too small an amount to form a 10% amalgam which Schnabel[15] mentions as being fluid.

At present, therefore, the best mechanism seems to be that of surface adhesion followed by only very slight solubility effects. The gold particles, after being coated with mercury, settle to the bottom under gravity. The nature of this solid phase has not been determined as yet, as mentioned earlier.

Summary

1. Amalgams as dilute as 0.3% have been prepared and analyzed, by a method described, with a precision approaching one part per thousand.
2. An improved type of apparatus is described for shaking the solubility tubes and sampling the amalgams.
3. Fifty-six determinations of the solubility of gold in mercury have been made with the tube described earlier (with slight modifications). The results are lower and the precision of measurement is much higher than those previously reported.
4. The bearing of the present data on the well-known amalgamation process for mining gold is briefly discussed.

ROCHESTER, NEW YORK

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[13] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Company, 1923, Vol. III, p. 497.

[14] Evans, "Metals and Metallic Compounds," Longmans, Green and Co., 1923, Vol. IV, pp. 113, 116.

[15] Schnabel, "Handbook of Metallurgy," Macmillan Co., New York, 1905, p. 924.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

CALCIUM PERCHROMATE. A NEW TYPE OF RED PERCHROMATE

BY J. A. RAYNOLDS AND J. H. REEDY

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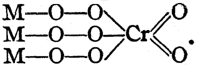
In spite of the very painstaking work of Riesenfeld[1], Wiede,[2] and others, our knowledge of the constitution of the perchromates is far from satisfactory. Their instability makes their isolation difficult, and no theory of the mechanism involved in their formation from chromates and peroxides has been advanced to prove their structure. The supposition that blue perchromic acid is formed in acid medium by a hyper-oxidation of chromates by means of hydrogen peroxide is hardly conclusive, when it is recalled that chromic acid is one of the strongest oxidizing agents and hydrogen peroxide in acid medium tends to behave as a reducing agent.

The red perchromates, which are formed when chromates and peroxides react in neutral medium, are more stable than the blue perchromic acid, and for this reason are better suited for isolation and analysis. Riesenfeld[3] has been the principal contributor to our knowledge of the red perchromates. From his analysis of the perchromates of the alkalies, he has proposed the type formula  $\begin{matrix}\text{M—O—O}\\ \text{M—O—O}\\ \text{M—O—O}\end{matrix}\!\!>\!\text{Cr}\!\begin{matrix}\nearrow\text{O}\\ \searrow\text{O}\end{matrix}$.

Experimental Part

Red Perchromic Acid.—A solution of what may be considered to be perchromic acid was prepared by the action at 0° of 30% hydrogen peroxide on freshly precipitated chromic hydroxide. The reaction is slow, an hour or more being required for its completion. The solution thus prepared has a brown to grape-juice color, and decomposes slowly upon standing at 0°, and very rapidly if the temperature is allowed to rise, giving a yellow solution of chromic acid. Up to this time, the product has not been isolated in a crystalline form. It is insoluble in organic solvents, and for this reason cannot be extracted from its water solution. Upon attempting to separate the excess water by freezing, the whole mixture congeals to a mushy mass. Upon acidification, the acid changes to the blue perchromic acid, and upon adding alkalies chromates are formed.

Calcium Perchromate.—This compound was first prepared by adding very slowly one volume of 30% hydrogen peroxide to three volumes of saturated calcium chromate, cooled to slightly below 0° by means of a bath of ice and salt. The mixture was allowed to stand at about −5° for an hour, and then the calcium salt was filtered off in a Gooch crucible. The product was washed with several portions of ice water, and finally with acetone, and dried on a clay plate in a desiccator. The yield was from 15 to 20% of the weight of the original calcium chromate.

Later it was found that calcium perchromate could be prepared by the action be-

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[1] Riesenfeld, *Ber.*, 38, 1885, 3059, 3380, 4068 (1905); 39, 3181 (1906); 41, 2826, 3536, 3941 (1908); 44, 147 (1911); *Ber. Naturforsch. Ges. Freiburg*, 17, 1 (1906); *Z. anorg. Chem.*, 74, 48 (1912).

[2] Wiede, *Ber.*, 30, 2178 (1897); 31, 516, 3139 (1898); 32, 378 (1899).

[3] Riesenfeld, *ibid.*, 41, 3947 (1908).

tween calcium acetate solution and the red perchromic acid as prepared above. The products obtained by these two methods are identical in every respect.

Calcium perchromate is a buff-colored, fluffy powder, slightly soluble in water with slow decomposition, and practically insoluble in ether, alcohol and acetone. It is stable at ordinary temperatures, but decomposes explosively at about 100°, leaving a greenish residue of calcium oxide and chromic oxide. The purity of the salt is indicated by the failure of its water solution to give a precipitate with barium or lead acetate solutions. Upon acidification, the blue perchromic acid is formed.

Calcium perchromate prepared in this way was analyzed as follows. The calcium was determined by dissolving about 0.2 g. in dilute hydrochloric acid and boiling to destroy any peroxides. The calcium was then precipitated as calcium oxalate, and determined by titration with standard potassium permanganate solution.

The chromium was determined as barium chromate by the following procedure. About 0.2 g. was dissolved in very dilute acetic acid, the solution heated to boiling, and the chromium reconverted into the chromate form by means of sodium peroxide. After neutralization with acetic acid, barium acetate was added, and the precipitated barium chromate was filtered, ignited and weighed.

The available (or peroxide) oxygen was determined by dissolving about 0.1 g. in a mixture of potassium iodide and dilute sulfuric acid solutions and titrating the iodine liberated with standard sodium thiosulfate solution.

The water of hydration was determined by passing a current of dried air over samples of about 0.2 g. heated in a combustion tube, and absorbing the moisture evolved in *a* Swartz tube containing magnesium perchlorate trihydrate. On account of the explosive nature of the material, the charge was distributed over the length of the tube, and the heating was started at one end of the tube and slowly extended toward the other end.

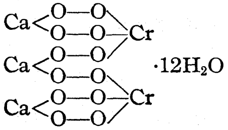
The results of these analyses have been collected in Table I.

TABLE I

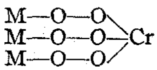
RESULTS OF ANALYSES

	Ca, %	Cr, %	Peroxide oxygen, %		H_2O, %	Oxygen (by difference), %
Experimental	18.74	16.37	15.27	15.19	34.56	
	18.70	16.42	15.25	15.26	34.46	
	18.69	16.34	15.21	15.23	34.49	
	18.70	16.39	15.22		34.57	
					34.43	
Average	18.71	16.38	15.23		34.50	15.17
Calcd. for $Ca_3Cr_2O_{12}\cdot 12H_2O$	19.01	16.45	15.18		34.18	15.18

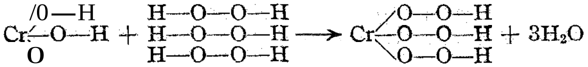
These analytical data indicate that the molecular formula for calcium perchromate is $Ca_3Cr_2O_{12}\cdot 12H_2O$. The only plausible configuration to represent this formula is



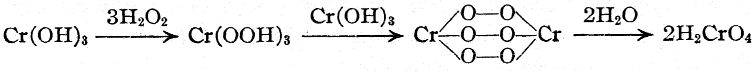
The type formula for univalent perchromates then should be



A very direct mechanism can be postulated to explain the formation of red perchromic acid:



The formation of chromic acid by the action of hydrogen peroxide on chromic hydroxide may, presumably, be represented



These methods are now being used to prepare other red perchromates, with a view to ascertaining if their formulas are analogous to that of the calcium salt.

Summary

1. A solution of red perchromic acid was prepared by the action of 30% hydrogen peroxide on freshly precipitated chromium hydroxide at temperatures near 0°.
2. Calcium perchromate is formed at low temperatures, either by the action of 30% hydrogen peroxide on saturated calcium chromate, or by the action between calcium acetate and red perchromic acid solutions.
3. Analysis of calcium perchromate indicates the formula, $Ca_3Cr_2O_{12}\cdot 12H_2O$.
4. A mechanism for the formation of chromates from chromium hydroxide by means of alkaline peroxides is suggested.

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[Contribution from the School of Chemistry of the University of Minnesota

SYNTHESIS OF PHOSGENE BY LIGHT AND BY ALPHA RADIATION

By Hubert N. Alyea[1] and S. C. Lind

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Extensive evidence shows that the initial step in a chemical reaction under alpha particle bombardment is ionization. In a great many reactions the subsequent formation of ion clusters[2] seemed sufficient to explain the resulting chemical reaction and yield per ion pair, which was in the neighborhood of two. Such a mechanism, involving ions, differs radically from the usual photochemical processes where the energy is insufficient for ionization. Among all the reactions studied, however, the union of hydrogen and chlorine was unique.[3] In this, many thousands of mole-

[1] National Research Fellow.

[2] S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," The Chemical Catalog Co., 1928, p. 139.

[3] S. C. Lind, *J. Phys. Chem.*, 16, 610 (1912); Le Radium, 9, 426 (1913); Bodenstein, *Z. Elektrochem.*, 22, 53 (1916); H. S. Taylor, This Journal, 37, 24 (1915); 38, 280 (1916); Porter, Bardwell and Lind, *ibid.*, 48, 2603 (1926).

cules react per ion pair produced by radon, and since this is an historically famous photochemical chain reaction, it seemed probable that while the primary step might be different (ionization by alpha particles *versus* photochemical excitation of the chlorine molecules), the subsequent mechanism involving an atomic chlorine chain was identical in the two cases. This has been decisively confirmed by the very recent work of Lind and Livingston,[4] proving that not only has the yield per ion pair the same value as the yield per quantum absorbed, but also that the two reactions have the same temperature coefficient.

Since this hydrogen–chlorine reaction bridged the gap between alpha particle and photochemical chain mechanisms, it seemed timely to investigate other photochemical chain reactions to ascertain how general this analogy might be. Such a study has been made on a number of reactions, and is reported elsewhere.[4a] The present paper deals with one of them: the formation of phosgene from moist carbon monoxide and chlorine.

No previous work has been done on the formation of phosgene under alpha particle bombardment and it is scarcely necessary to review here the literature on the photochemical formation.[5] Suffice it to state that the photochemical formation is a chain reaction at least several thousand molecules in length,[3,5] and to emphasize, in particular, that the reaction rate is proportional to the square root of the number of quanta absorbed. It is generally accepted that the latter is an indication of an atomic chlorine chain mechanism,[6] and the question immediately arises whether the alpha particle reaction will give rise to atomic chlorine chains, and exhibit similar kinetics. This has been the objective of the present research.

Theoretical

The experimental conditions and calculations necessary for establishing the identity of the kinetics subsequent to the two types of activation in the reaction

$$CO + Cl_2 \longrightarrow COCl_2$$

are as follows: the kinetics of the photochemical reaction have been expressed by[3,5,6]

$$\frac{+dP_{COCl_2}}{dt} = K_p\sqrt{I_{abs.}}\cdot\sqrt{P_{CO}}\cdot P_{Cl_2} \qquad (1)$$

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[4] Lind and Livingston, THIS JOURNAL, 52, 593 (1930).

[4a] THIS JOURNAL, forthcoming.

[5] See in particular the recent series of papers by Bodenstein, Part I, M. Bodenstein, *Z. physik. Chem.*, 130, 422 (1927); Part II, J. Schumacher, *ibid.*, 129, 241 (1927); Part III, Bodenstein and Onoda, *ibid.*, 131, 153 (1927); Part IV, *ibid.*, 3B, 459 (1929). See also Bodenstein, *ibid.*, 85,373 (1913); Davy, *Phil. Trans.*, 101, 144 (1812); Weigert, *Ann. Physik*, 24,243 (1907); Bonhoeffer, *Z. Physik*, 13, 94 (1923); Coehn and Becker, *Ber.*, 43, 130 (1910); and the review and bibliography of Kistiakowsky in "Photochemical Processes," The Chemical Catalog Co., Inc., New York, 1928, pp. 100–102.

[6] Bodenstein, Refs. 3 and 5, and *Sitzb. preuss. Akad. Wiss.*, 13, 114 (1926).

and the corresponding alpha particle reaction would be

$$\frac{+\mathrm{d}P_{\mathrm{COCl_2}}}{dt} = K_1\sqrt{i_p}\cdot\sqrt{P_{\mathrm{CO}}}\cdot P_{\mathrm{Cl_2}} \qquad (2)$$

in which the number of ion pairs, i_p, corresponds to the number of excited molecules produced photochemically, I_{abs}. Furthermore, $i_p = (i_{\mathrm{CO}}P_{\mathrm{CO}} + i_{\mathrm{Cl_2}}P_{\mathrm{Cl_2}})E_t$, in which i is specific ionizations, 1.00 for CO and 2.42 for Cl_2,[7] P is partial pressures, and E_t is number of curies of radon present.[8]

If the analogy is complete, the alpha reaction would he proportional to the square root of the radon concentration, which would give evidence of an atomic chlorine chain mechanism as discussed above. For simplicity in calculation, this was measured when the carbon monoxide pressure was the same as the chlorine pressure, *i*. e., where $P_{\mathrm{CO}} = P_{\mathrm{Cl_2}} = (P_{\mathrm{CO}} + P_{\mathrm{Cl_2}})/2$. Under such conditions, if $P = P_{\mathrm{CO}} + P_{\mathrm{Cl_2}}$, we have from Equation 2 above

$$\frac{+\mathrm{d}P_{\mathrm{COCl_2}}}{dt} = -{}^1/_2\,\frac{\mathrm{d}P_{\mathrm{CO+Cl_2}}}{dt} = K_1\sqrt{(1.00\,P_{\mathrm{CO}} + 2.42\,P_{\mathrm{Cl_2}})E_t}\,.\,\sqrt{P_{\mathrm{CO}}}\cdot P_{\mathrm{Cl_2}} =$$

$$K_1\sqrt{\frac{3.42}{2}\cdot P\cdot E_t}\cdot\sqrt{\frac{P}{2}}\cdot\frac{P}{2} = \frac{\sqrt{3.42}}{4}K_1\sqrt{E_t}\,P^2 \qquad (3)$$

The radon concentration E_t remained essentially constant under the normal experimental run of thirty minutes, and can be treated as a constant. In such a case, integrating Equation **3**, we obtain

$$K_1 = \frac{4}{2\sqrt{3.42}\,\mathrm{d}t\sqrt{E_t}}\int_{P_1}^{P_2}\frac{\mathrm{d}P}{P^2} = \frac{1.0815\,(1/P_2 - 1/P_1)}{\mathrm{d}t\sqrt{E_t}} \qquad (4)$$

where K_1 is the velocity constant for the alpha particle reaction. K_1 has been evaluated in the following results over an eighty-three-fold variation of the amount of radon and hence of the intensity of alpha radiation.

Our next step is to test kinetic Equation 2 by varying the carbon monoxide to chlorine ratio. Defining $k = P_{\mathrm{Cl_2}} - P_{\mathrm{CO}}$, three cases present themselves with the following solutions.

Case 1.—Where $k > 0$, **i**. e., where $P_{\mathrm{Cl_2}} > P_{\mathrm{CO}}$, from Equation 2

$$\frac{+\mathrm{d}P_{\mathrm{COCl_2}}}{\mathbf{dt}} = -\frac{\mathrm{d}P_{\mathrm{CO}}}{dt} = K_1\sqrt{i_p}\sqrt{P_{\mathrm{CO}}}\,.\,(P_{\mathrm{CO}} + k)$$

and therefore

$$\frac{-\mathrm{d}P_{\mathrm{CO}}}{(P_{\mathrm{CO}} + k)\sqrt{P_{\mathrm{CO}}}} = K_1\sqrt{i_p}\cdot\mathrm{d}t \qquad (5)$$

Considering $\sqrt{i_p}$ as constant during each successive interval (see Col. 5, Table IV) and integrating, we obtain

$$-\left[\frac{2}{\sqrt{k}}\tan^{-1}\sqrt{\frac{P_{\mathrm{CO}}}{k_1}}\right]_{P_1}^{P_2} = K_1\int\sqrt{i_p}\cdot\mathrm{d}t$$

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[7] *i for chlorine,* 2.42. *See Porter,* Bardwell *and Lind, Ref.* **3.**

[8] *As is sometimes allowable* in *alpha particle calculations,* only ***the*** *ionization on the reactants is considered. See S. C. Lind,* **Ref.** 2, **p.** 100.

and since

$$\sqrt{i_p} = \sqrt{(1.00\,P_{CO} + 2.42\,P_{Cl_2})E_t} = \sqrt{(3.42\,P_{CO} + 2.42\,k)E_t}$$

we have

$$K_1 = \frac{\frac{\pi}{60 \times 180} \times \frac{2}{\sqrt{k}}\left[\tan^{-1}\sqrt{\frac{(P_{CO})_2}{k}} - \tan^{-1}\sqrt{\frac{(P_{CO})_1}{k}}\right]}{\int dt\,\sqrt{i_p}} =$$

$$\frac{5.82 \times 10^{-4}\left[\tan^{-1}\sqrt{\frac{(P_{CO})_2}{k}} - \tan^{-1}\sqrt{\frac{(P_{CO})_1}{k}}\right]}{\int dt\,\sqrt{k}\,\sqrt{(3.42\,P_{CO} + 2.42\,k)E_t}} \tag{6}$$

Case 2.—Where **k** $= 0$, *i. e.*, where $P_{Cl_2} = P_{CO} = (P_{CO} + P_{Cl_2})/2 = P/2$. This has been discussed above, Equation 4, where K_1 is evaluated.

Case 3.—Where **k** < 0, **i.** *e.*, where $P_{Cl_2} < P_{CO}$. Let $k' = -k = P_{CO} - P_{Cl_2}$. As in Equation 5, Case 1, we obtain

$$\frac{-dP_{CO}}{(P_{CO} - k')\,\sqrt{P_{CO}}} = K_1\,\sqrt{i_p}\cdot dt \tag{7}$$

in which

$$\sqrt{i_p} = \sqrt{(1.00\,P_{CO} + 2.42\,P_{Cl_2})E_t} = \sqrt{(3.42\,P_{CO} - 2.42\,k')E_t}$$

Expression 7 integrates into

$$K_1 = \frac{2.3026\left[\log\frac{\sqrt{P_2} - \sqrt{k'}}{\sqrt{P_2} + \sqrt{k'}} - \log\frac{\sqrt{P_1} - \sqrt{k'}}{\sqrt{P_1} + \sqrt{k'}}\right]}{\int dt\,\sqrt{k'}\,\sqrt{(3.42\,P_{CO} - 2.42\,k')E_t}} \tag{8}$$

K_1 has been evaluated experimentally in this paper for the three cases.

Returning to Equations 1 and 2, it remains to evaluate $\frac{\text{yield per ion pair}}{\text{yield per quantum}}$ Considering only the case where $P_{CO} = P_{Cl_2} = P/2$, let under the experimental conditions used: q = number of quanta absorbed at $P = 760$ mm. CO + Cl_2 and N = number of ion pairs produced at P = 760 mm. CO + Cl_2. Assume that $Pq/760$ = number of quanta absorbed at pressure P of CO + Cl_2,[9] let x = number of quanta equivalent to one ion pair. Substituting these values in Equation 2, we obtain

$$\frac{+dP_{COCl_2}}{dt} = \frac{-\tfrac{1}{2}dP_{CO+Cl_2}}{dt} = K_1\sqrt{i_p + \frac{q_{abs}}{x}}\cdot\sqrt{P_{CO}}\cdot P_{Cl_2} =$$

$$K_1\sqrt{\frac{NP}{760} + \frac{qP}{760\,x}}\cdot\sqrt{P_{CO}}\cdot P_{Cl_2}$$

Letting $K_2 = K_1/760 \times 2$, and integrating, we have

$$K_2 = \frac{2K_1}{2\sqrt{760 \times 2}} = \left(\frac{1}{dt\,\sqrt{N + q/x}}\right)\int_{P_1}^{P_2}\frac{dP}{P^2} = \frac{1/P_2 - 1/P_1}{dt\,\sqrt{N + (1/x)}} = \frac{k_{\alpha+L}}{dt\,\sqrt{N + (q/x)}}$$

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[9] Incomplete light absorption. This simplifying assumption introduces an error, by not applying Lambert's law, which is less than 30% even in the most unfavorable experimental run in this paper. The error is small because $q_{abs.}$ and the photochemical rate were measured in the same region of chlorine pressure, and the pressure changes less than 30% during a light run.

The experimental method was to measure (1) alpha rate alone, (2) alpha plus light rate, during a single run with the same gas mixture. This gives the following solution for x, the number of quanta necessary to produce as much reaction as one ion pair

$$\frac{\text{Velocity}_{\text{alpha + light}}}{\text{Velocity}_{\text{alpha alone}}} = \frac{k_{\alpha+\mathrm{L}}}{k_\alpha} = \frac{\sqrt{N + (q/x)}}{\sqrt{N}}$$

Solving for x, we obtain

$$x = \frac{q}{N\left[\left(\frac{k_{\alpha+\mathrm{L}}}{k_\alpha}\right)^2 - 1\right]} \tag{9}$$

Or, for a comparison between (1) alpha rate alone, and (2) light rate alone, we have

$$\frac{k_\mathrm{L}}{k_\alpha} = \frac{\sqrt{q/x}}{\sqrt{N}} \text{ or } x = \frac{q}{N(k_\mathrm{L}/k_\alpha)^2} \tag{10}$$

This paper determines these values of x experimentally.

Experimental

The reaction vessel M, Fig. 1, was a pyrex bulb about 4 cm. in diameter, the pressure in which was indicated by the quartz spiral manometer V.[10] Alpha particles were supplied through the usual type of radon bulb *a*.[11] The stopcocks were treated with a special chlorine-resisting lubricant.[12] The evacuating system, H, consisted of a liquid-air trap, a refluxing mercury bath as a trap for chlorine, a McLeod gage, a mercury vapor pump and finally the oil pump, connected with the reaction vessel at H in the order named. The water pump, I, was used for removing chlorine-rich gases. Immediately before a run the reaction apparatus was flushed out five times by evacuating to 10^{-2} mm. of mercury, and filling with carbon monoxide through F. It was then evacuated to 10^{-3} mm. of mercury and chlorine admitted through valve J, until the spiral manometer indicated the partial chlorine pressure desired. The tubing between stopcocks F, G, J and K was then flushed out with carbon monoxide by several evacuations. Finally, carbon monoxide was allowed to flow in until the mixture of gases registered about an atmosphere pressure. K was immediately closed (time = 0), and pressure and temperature readings were taken every minute to follow the drop in pressure of the gases caused by the formation of phosgene from chlorine and carbon monoxide under alpha particle bombardment.

Carbon monoxide, purer than 99.7%,[13] was obtained by running c. p. 90% formic acid into concentrated sulfuric acid. Gentle heating of the generator, B, greatly accelerated the evolution of gas. Carbon dioxide was removed by the potassium hydroxide in vessel C. Initially the carbon monoxide apparatus was evacuated and thoroughly swept out with fresh carbon monoxide many times, and during the subsequent six months of measurements the apparatus was never again exposed to the air, since the generator could be nearly emptied by applying suction at A and recharged with fresh sulfuric acid without admitting any air. The carbon monoxide was freshly prepared about an hour before each run, and was delivered to the reaction vessel through

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[10] Bodenstein, *Z. Elektrochem.*, 22, 331 (1916).

[11] Lind and Bardwell, THIS JOURNAL, 45, 2586, 2593 (1923).

[12] H. N. Stephens, *ibid.*, 52, 635 (1930), to whom the authors are indebted.

[13] *Cf.* Bodenstein and Plaut, *Z. physik. Chem.*, 110, 401 (1924).

stopcock F by proper manipulation of stopcock D, controlling the potassium hydroxide solution in the storage bulb, E.

The chlorine was prepared according to the method described by Marshall.[14] Tank chlorine was bubbled through a tall water column, then through a tube at 260° packed with powdered glass to dissociate chlorine oxides and finally frozen out with liquid air. It was then redistilled under high vacuum, four times at −119° (ethyl bromide) into a receiver immersed in liquid air. The apparatus in the last two distillations and final storage bulbs had been thoroughly baked out in vacuo. They held at 5×10^{-6} mm. for more than six hours. During a single collection two two-liter storage bulbs were filled with chlorine at two atmospheres pressure, which sufficed for about fifty runs. The chlorine gas was delivered to the reaction vessel through a specially constructed capillary, J, described elsewhere,[15] which permitted the removal of small samples from time to time without contaminating the main gas supply.

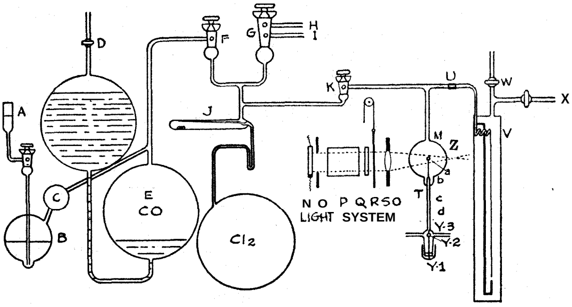

Fig. 1.—A, formic acid; B, sulfuric acid; C, KOH washing system, consisting of a tube of solid KOH, and several flasks of concentrated KOH solutions; E, carbon monoxide storage tank; H, to evacuating system; I, to water pump; J, special chlorine valve; M, reaction vessel; N, mercury Lab-arc lamp;* O, screens for definition of light beam; P, 5-cm. filter of 5% $CuSO_4$ solution; Q, Corning glass filter, G585;* R, shutter; S, lens; T, capillary to radon bulb; U, pyrex to quartz seal; V, quartz manometer, W, to suction pump; X, to mercury manometer; Y, to mercury level regulator; Y-1, nickel cup holding mercury seal around stuffing box; Y-2, hole in rod for holding and breaking radon capillary; Y-3, rod hollowed out for flexibility—holds mercury in capillary at fixed level; Z, focus of light; a, neck of alpha bulb; b, c, d, marked calibrated levels on capillary T.

* We are indebted to Dr. Stenstrom for the use of the Lab-arc, and to Dr. G. L. Glockler for the Corning glass filter.

In some runs it was desired to vary the radon concentration; this was accomplished by the device shown in T, Fig. 1. The volume of the small bulb to a, and of the capillary to marks b, c and d were obtained by measuring the loss in weight of a container from which mercury was sucked into the capillary up to the various marks. Accuracy

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[14] Marshall, J. *Phys. Chem.*, 30, 760 (1926).

[15] Alyea, This Journal, 52, 1936 (1930).

was within 1%. The volume of the bulb was 0.00322 cc., the volume of the bulb and capillary to mark d, 0.0218 cc. By raising the mercury level to marks a, b, c or d, the volume occupied by the radon, and its subsequent pressure in the alpha bulb, could be varied. Since only the walls of the alpha bulb itself are thin enough to permit the passage of the alpha particles into the reaction sphere, this is a simple method for varying the effective radon concentration. For simplicity, in the tables which follow, only the *effective radon concentration* is given, that is, E_t is the radon present only in the bulb itself, disregarding how much radon may be in the capillary due to different mercury level settings. Unfortunately, measurements cannot be made until four hours after a new setting of the mercury level in the capillary[11] since Rn, RaA and RaC′, the sources of the alpha particles, must come to equilibrium. While this prevents making measurements on the same gas at different radon concentrations, fresh samples of gas gave reasonably reproducible results.

The apparatus used for the photochemical runs, N to S, Fig. 1, is self-explanatory. Spectral photographs of the light entering the reaction vessel, M, showed that the 3660 Å. mercury line comprised a large proportion of the light energy. The remaining 20% was also calculated in as if it were 3660 Å., since it was composed of approximately equal intensities of the 3130 Å. and 40404070 Å. mercury lines. The light radiation was expressed finally as the number of quanta absorbed in the reaction sphere by half an atmosphere of chlorine. For the calibration, the light energy was compared with a standard lamp, using a Moll thermopile. The cone of the thermopile received the light at point Z, Fig. 1. The galvanometer deflections were obtained for the light beam before and after its passage through the empty bulb, and through the bulb filled with chlorine at different pressures. There was no absorption with carbon monoxide. When the photochemical reactions were completed, the half of the bulb farthest from the light source was cut away, and the light coming through the remaining half of the bulb was measured. Similar measurements were made on the half of the bulb which had been cut away. These data enabled us to calculate in several different ways the original intensity of the beam, the percentage of light absorbed by, or reflected from, the walls of the reaction bulb and finally the number of quanta absorbed by the chlorine in the bulb.

In practice the normal alpha rate at equal carbon monoxide and chlorine pressures was measured for a few minutes and then the shutter R, shielding the reaction vessel from the ultraviolet light, was raised and pressure readings on the combined alpha and photochemical rates were taken at half-minute intervals. Five minutes later the shutter was dropped and once more the alpha rate alone was measured. The radon concentration and light intensity were so chosen as to give an alpha particle reaction several fold slower than the photochemical one, both to enhance the accuracy in measuring the photochemical reaction, and to prevent too much gas reaction before the photochemical measurements were begun.

In a few runs the experimental procedure was reversed, the photochemical–alpha reaction coming first, followed by the alpha alone, and finally checked by a second photochemical–alpha series of measurements.

Results

At Different Radon Concentrations.—Two typical runs are given in Table I. K_1 is calculated from Equation 4. In Run **36** and all runs at high radon concentrations an induction period, corresponding to the usual photochemical "clean up" of impurities in chain reaction,[16] is very

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[16] Cf. Bodenstein, Refs. 3, 5 and 10, and Burgess and Chapman, J. *Chem. Soc.*, *89*, 1402 (1906).

evident. It is not noticeable, however, in Run 42 and similar runs at low radon concentrations. The smaller concentrations are undoubtedly unable to clean up the impurities during the first few minutes, and hence the induction period extends over the greater part of the run. The error so introduced was minimized by comparing velocity constants over the same initial pressure drops in the various runs (about 100 mm.), assuming the relations during the induction period to be the same as those obtaining afterwards. Thus in Run 36, the value 6.2 and not 7.2 was taken as the velocity constant, while 5.3 was used for Run 42. It is seen that the

TABLE I

SYNTHESIS OF PHOSGENE AT TWO DIFFERENT INTENSITIES OF ALPHA RADIATION

Run 36. **Temp.,** 27°. E_t = 0.00834 **curie**

Time, minutes	Pressures Total	Phosgene	Pressure $CO + Cl_2$ $(=P)$	$1/P$	$\frac{(1/P_2 - 1/P_1) \times 1.0815}{At\sqrt{E_t}} = K_1 (\times 10^4)$
0	724.0	0.0	724.0	0.001381	3.2
1	717.0	7.0	710.0	1408	3.5
2	710.0	14.0	696.0	1437	5.6
3	699.0	25.0	674.0	1484	6.7
4	686.7	37.3	649.4	1540	6.8
5	675.0	49.0	626.0	1597	8.0
6	662.5	61.5	601.0	1664	7.8 (× 2)
8	640.9	83.1	557.8	1793	
				Average to 8 **min.,**	6.2
9	631.3	92.7	538.6	1857	7.6
10	321.9	102.1	519.8	1924	8.0
11	613.0	111.0	502.0	1992	8.1
13	596.8	127.2	469.6	2129	8.2 (X 2)
14	589.8	134.2	455.6	2195	7.9
15	583.6	140.4	443.2	2256	7.3
21	550.9	173.1	377.8	2647	7.7 (× 6)
				Average to 21 **min.,**	7.2

Run 42. **Temp.,** 27°. E_t = 0.000101 **curie**

Time, minutes	Pressures Total	Phosgene	Pressure $CO + Cl_2$ $(=P)$	$1/P$	$K_1 (\times 10^4)$
(−0.5)	(709.6)	0.0	(709.6)	0.001409	...
0	709.4	0.2	709.2	1410	6.0
6	701.4	8.2	693.2	1443	4.7
12	695.1	14.5	680.6	1469	4.7
18	689.3	20.3	669.0	1495	4.9
24	683.3	26.3	657.0	1522	4.9
30	677.6	32.0	645.6	1549	4.7
36	672.2	37.4	634.8	1575	5.2
42	666.6	43.0	623.6	1604	6.4
47	661.0	48.6	612.4	1633	6.2
58	649.6	60.0	589.6	1696	
				Average to 58 **min.,**	5.3

$$\frac{E_{t(\text{Run 36})}}{E_{t(\text{Run 42})}} = \frac{0.00834}{0.000101} = \frac{83}{1}$$

velocity constant, calculated by assuming the reaction rate proportional to the one-half power of the radon concentration, is essentially the same in both runs, although the radon concentration has been varied eighty-three-fold (0.00834/0.000101). Table II summarizes the runs at different radon concentrations. In the seventh column, K_1 has been calculated from $K_1 = (1/P_2^{3/2} - 1/P_1^{3/2})/\Delta t E_t$, an expression derived by the same reasoning as in Equation 4, only that it assumes that the reaction is proportional to the first power of the radon concentration. From the last two columns it is at once evident that the reaction is proportional to the one-half and not to the first power of the radon concentration.

TABLE II

VELOCITY CONSTANT. PHOSGENE FORMATION UNDER ALPHA PARTICLE BOMBARDMENT AT DIFFERENT RADON CONCENTRATIONS

Run	E_t, av. radon concn. during run in curie	Pressure, mm. CO + Cl_2 Initial, P_1	Final, P_2	Time, dt, elapsed, min.	$\sqrt{E_t}$	Values for K_1 ($\times 10^4$) Based[a] on E_t	Based[b] on $\sqrt{E_t}$
42	0.000101	709.2	589.6	58	0.01005	23.0	5.3
41	0125	694.2	635.0	24	.01181	31.0	6.3
45	0292	670 2	603.2	18	.01709	19.0	5 9
34	0413	713.5	622 5	18	,02032	16.2	6.1
33	0422	549.4	424.2	36	.02054	24.0	7.9
55	3740	698.9	588.1	6	.06116	7.1	7.9
44	656	719.6	597.4	5	.08099	5.1	7.6
43	660	684.6	594.2	4	.08124	5 0	7.4
36	834	724.0	557.8	8	.09132	3.8	6.2
35	839	703.5	562.5	5	.09160	5 1	8.4
						Average,	6.9

$P_{CO} = P_{Cl_2}$. Volume of reaction sphere, 49.2 cc. Temperature, 27°

[a] Here $K_1 = \frac{(P_2^{-3/2} - P_1^{-3/2})}{\Delta t E_t}$.
[b] Here $K_1 = \frac{(1/P_2 - 1/P_1) \times 1.0815}{\Delta t \sqrt{E_t}}$.

Variation of the Chlorine–Carbon Monoxide Ratio.—Tables III and IV show values of K_1 with one or the other gas in excess. Table V is a summary of the various runs, and shows that K_1 is essentially constant over a range of carbon monoxide pressures from 638.5 to 162.8 mm., the corresponding chlorine pressures having been increased from 95.5 to 587.1 mm. Runs 49 and 51 indicate that at still lower pressures of carbon monoxide the constant probably falls off. K_1 is calculated for the first seven minutes of a run, using about 0.005 curie of radon (Col. 4). This gives experimental conditions identical with certain runs in Table II, and makes the values in Tables II and V strictly comparable. If K_1 in Table V is taken over very long time intervals, the values are all about 20% higher, a fact which may be attributed both to the induction period and to the inaccuracy of our original kinetic equation in taking care of certain secondary factors in the phosgene reaction.

TABLE III

ALPHA RAY SYNTHESIS OF PHOSGENE IN EXCESS OF CARBON MONOXIDE

Run 53. **Temperature,** 27°. P_{CO} **initial,** 542.4 **mm.** P_{Cl_2} **initial,** 199.2 mm. $k = P_{Cl_2} - P_{CO} = 343.2$. E_t, 0.00389 **curie.**

Time	Total	Pressure, mm. Phosgene	CO	$\sqrt{3.42CO-2.42k}$ (av. value)	log A/B $= \log \frac{\sqrt{P} - \sqrt{k}}{\sqrt{P} + \sqrt{k}}$	(log A/B)$_2$ − (log A/B)$_1$	$K_1^a \times 10^4$
0	741.6	0	542.4	31.9	1 05631	662	4.1
1	737.9	3.7	538.7	31.7	0.04969	1902	6.0 (X 2)
3	727.4	14.2	528.2	31.2	.03067	868	5.6
4	723.0	18.6	5238	30.9	,02199	856	5.6
5	718.6	23.0	519.4	30.6	.01343	977	6.4
6	713.8	27.8	514.6	30.4	.00366	1005	6.6
7	709.2	32.4	510.0	. . .	.99361	. .	. .
						Average to 7 **min.,**	5.8
9	698.9	42.7	499.7	29.9	0.97047	2314	7.8 (X 2)
11	690.9	50.7	491.7	29.4	.95187	1860	6.2 (X 2)
13	6827	58.9	483.5	29.0	.93107	2080	7.6 (X 2)
15	675 3	66 3	476.1	28 5	.91118	1989	7.0 (X 2)
17	668.5	73.1	469.3	28.1	.89205	1913	6.6 (X 2)
21	659.1	82.5	459.9	27.6	.86279	2926	5.4 (X 4)
						Average to 21 **min.,**	6.3

$$^{a}\ K_1 - \frac{2.3026 \times (\lg_2 - \lg_1)}{At\sqrt{E_t}\sqrt{k}\sqrt{3.42CO - 2.42k}}$$ **see Equation** 8.

TABLE IV

ALPHA RAY SYNTHESIS OF PHOSGENE IN EXCESS OF CHLORINE

Time	Total	Pressure, mm Phosgene	Carbon monoxide, P	$\sqrt{3\ 42P+2\ 42k}$	$\sqrt{P/k}$	tan-' $\sqrt{P/k}$ (C)	$C_2 - C_1$	K_1^a (× 10^4)
0	735.1	0.0	226.1	1459	0 895	51°50′	39'	5.0
1	725.4	9.7	216.4	1426	.875	41 11	99.5	6.5 (X 2)
3	701 6	33.5	192.6	1343	.825	39 31.5	43.5	5.9
4	692.1	43.0	183.1	1310	.804	3848	59	7.9
5	679.4	55 7	170.4	1267	.776	37 49	55	7.5
6	668 8	66.3	159.8	1230	.751	36 54	55	7.6
7	658.6	76.5	149.6	1176	.727	35 59	59	
							Av. to 7 min.,	6.7
8	647.8	87.3	138.8	1158	0.700	3500	56	8.4
9	638.6	96.5	129.6	1127	.676	3404	60	8.0
10	628.9	106.2	119.9	1093	.651	3304	61	8.7
11	619.7	115.4	110.7	1062	.626	3203	58	9.0
12	611.5	123.6	102.5	1035	.603	31 05	61	8.7
13	603.8	131.3	94.8	1008	.579	30 04	59.5	9.3
14	596.8	138.3	87.8	984	.556	29 04.5	60.5	9.1
15	589.6	145.5	80.6	960	.533	28.04	126	9.5
17	576.0	159.1	67.0	912	.487	25 58	90	9.7 (X 2)
19	567.6	167.5	58.6	885	.455	2428	98	7.2 (X 2)
21	559.0	176.1	50.0	855	.421	2250	80	8.1 (X 2)
							Av. **to** 21 **min.,**	8.0

TABLE IV (Concluded)

	Pressure, mm.							
Time	Total	Phosgene	Carbon monoxide, P	$\sqrt{3.42P+2.42k}$	$\sqrt{P/k}$	$\tan^{-1}\sqrt{P/k}$ (C)	C_2-C_1	$K_1{}^a$ ($\times 10^4$)
23	552.8	182.3	43.8	833.5	394	2130	96	6.7 (× 2)
25	546.0	189.1	37.0	810.5	.362	19 54	64	8.2 (× 2)
27	541.9	193.2	32.9	796.5	.341	18 50	115	5.5 (× 2)
30	535.1	200.0	26.1	773.2	.304	1655	(30 × 28)	6.6 (× 3)
60	509.8	225.3	0.8	686.7	053	3 01		5.2 (× 30)

Run 48. E_t, 0.00508 **curie. Initial** P_{Cl_2}, 509.0 **mm. Initial** P_{CO}, 226.1 **mm.** $k = P_{Cl_2} - P_{CO} = 282.9$ mm.

$$^{a}\ K_1 = \frac{5.82 \times 10^{-4}\ (\tan^{-1}\sqrt{P_{2CO}/k} - \tan^{-1}\sqrt{P_{1CO}/k}}{\sqrt{k} \times \Delta t \times \sqrt{3.42P_{CO} + 2.42k} \times \sqrt{E_t}}.$$

TABLE V

SUMMARY OF VELOCITY CONSTANTS FOR PHOSGENE FORMATION UNDER ALPHA PARTICLE BOMBARDMENT AT DIFFERENT INITIAL PRESSURES OF CARBON MONOXIDE AND OF CHLORINE

	Initial pressures				
Run	Carbon monoxide	Chlorine	Et	$k = P_{Cl_2} - P_{CO}$	K_1 ($\times 10^4$)
	Where $k < 0$, K_1 **evaluated by Equation** 8				
54	638.5	95.5	0.00384	−543.0	8.6
47	620.2	138.3	514	−481.9	9.3
56	604 5	137.0	369	−467.5	8.2
53	542.4	199.2	389	−343.2	5.8
52	505.0	235.7	422	−269.3	6.3
41	434.2	300.0	0.125	−134.2	5.8
46	382.0	352.0	530	− 30.0	7.1
	Where $k = 0$, K_1 **evaluated** by **Equation** 4, **see Table** II				
55	349.5	349.5	0.00374	0.0	7.9
44	359.8	359.8	656		7.6
43	352.5	352.5	660		7.4
36	362.0	362.0	834		6.2
35	365.8	365.8	939		8.4
	Where $k > 0$, K_1 **evaluated** by **Equation** 6				
48	226.1	509.0	0.00508	+282.9	6.7
50	162 8	587.1	463	$424.3	5.1
				Average,	7.2
49	107.8	649.5	0.00468	$5417	(3.1)
51	51.1	684.4	442	$633.3	(0.58)

Quantum Efficiency Versus Yield per **Ion** Pair.—The first step in such a comparison was the calibration of the radiation intensities. The alpha radiation was calculated as the number of ion pairs produced per minute per curie of radon for a mixture of 380 mm. of chlorine and 380 mm. of carbon monoxide. Experimentally it involved evaluating the ionizing power of the alpha ray bulb, by measuring the velocity of a chemical reaction (the synthesis of water from electrolytic gas) for which the ratio of ionization to chemical reaction is known, carried out in the identical apparatus used for the phosgene reaction. The experimental procedure and calculations appear in the literature,[17] and the velocity constant $(k\mu/\lambda)^1 = [\log (P_1/P_2)]/[E_0 (e^{-\lambda t_1} - e^{-\lambda t_2})]$, where P is the pressure of hydrogen plus oxygen, had the experimental value of 2.03 in our apparatus. The volume of the reaction sphere was 49.2 cc. Since $(k\mu/\lambda)^1$ is "the number of times a given volume will completely react at any given pressure held constant during the decay of one curie of radon (5.55 days, average life) if the radon content were maintained constant,"[18] the number of molecules which reacted per minute, with one curie of radon under the experimental conditions, was

$$\frac{2.03 \times 49.2}{5.55 \times 24 \times 60} \times 2.46 \times 10^{19} = 3.08 \times 10^{16} \text{ molecules}$$

where 2.46×10^{19} is the number of molecules in one cubic centimeter of gas at 760-mm. pressure and 27°. Now for each ion pair six molecules react,[19] forming four molecules of water, and therefore the number of ion pairs formed per minute was $3.08 \times 10^{17}/6 = 5.13 \times 10^{16}$ ion pairs. The specific ionization in a gas mixture of chlorine and carbon monoxide at equal pressures, $i_{CO + Cl_2}$, is 171.0; and that in electrolytic gas, $i_{2H_2 + O_2}$ is 52.7. Hence *the total number of ion pairs produced in the chlorine–carbon monoxide mixture at 760-mm. pressure and 27° per curie of radon per minute* is $5.13 \times 10^{16} \times (171.0/52.7) = 1.66 \times 10^{17}$ ion pairs. Strictly speaking, the water synthesis should be made at pressures more than three times (171.0/52.7) greater than the phosgene runs, in order to have identical paths of ionization.[3] However, the size of the reaction vessel[20] permitted the standardization to be made at the same pressures, a fact experimentally verified when several runs made on phosgene at one-third of an atmosphere gave approximately the same velocity constant as at one atmosphere.

The light radiation was expressed as the number of quanta absorbed in the reaction vessel per minute by a gas mixture of 380 mm. of chlorine and 380 mm. of carbon monoxide. The standard lamp calibrated by the Bureau of Standards for 0.25, 0.30 and 0.35 ampere gave galvanometer deflections on a scale about 2.5 meters distant which corresponded to the following ergs of energy falling on the thermopile per minute per centimeter deflection on the scale: 1810, 1820 and 1780, giving an average of 1800 ergs. Comparable measurements on the light entering the reac-

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[17] Lind and Bardwell, THIS JOURNAL, 45, 2585 (1923).

[18] S. C. Lind, Ref. 2, p. 123.

[19] See S. C. Lind, THIS JOURNAL, 41, 531–559 (1919). In this paper, read before the American Chemical Society at Minneapolis, September 11, 1929, the error of dividing by four instead of by six led to the ratio of quantum efficiency: yield per ion pair of 0.5 instead of 0.78 as given in Table VII.

[20] Bardwell and Doerner, *ibid.*, 45, 2594 (1923).

tion vessel were then made. It was composed of 3600 Å., one quantum of which has ch/λ in cm. = $(3 \times 10^{10} \times 6.55 \times 10^{-27})/(3660 \times 10^{-8}) = 5.36 \times 10^{-12}$ ergs of energy, where 3×10^{10} is the velocity of light in cm. per second and 6.55×10^{-27} is the value of the Planck constant h. One centimeter deflection on the galvanometer scale, therefore, represented $1800/5.36 \times 10^{-12} = 3.35 \times 10^{14}$ quanta per minute. As mentioned earlier in the paper, the amount of light absorbed by and reflected from the walls of the reaction vessel, about 30% of the total light, was checked in several ways. The following is a great simplification of the actual data, but will suffice to show the experimental value obtained: (1) galvanometer deflection from the light entering the gas mixture after passing through the first wall of the reaction vessel, 15.2 cm.; (2) calculated galvanometer deflections after passage through (1) and 380 mm. of chlorine, 0.40 cm.; **(3)** calculated galvanometer deflection absorbed by 380 mm. of chlorine, or by a mixture of 380 mm. of chlorine plus 380 mm. of carbon monoxide, 14.8 cm. The deflection of 14.8 cm. represents $14.8 \times 3.35 \times 10^{14} = 4.95 \times 10^{15}$ *quanta per minute absorbed* by the chlorine–carbon monoxide gas mixture at 760-mm. pressure in the reaction vessel.

The results of a combined alpha particle–photochemical run made under these conditions of radiation are given in Table VI, where it is seen how the velocity constants for the run have been calculated. Table VII summarizes all of the runs. The final column calculates that 0.78 quanta produce as much reaction as one ion pair. The fact that this ratio remains approximately constant when the absolute rates have been cut down four-fold by the addition of oxygen is particularly interesting in the light of the recent studies of Bodenstein[5] where it was shown that at even these small oxygen concentrations the oxidation of carbon monoxide, photosensitized by chlorine, plays a prominent role. There is little doubt but that the photochemical reactions which he postulates between oxygen, chlorine and carbonyl chloride are taking place in the alpha particle reaction as well. The value 0.78, however, is at least 20% lower than the true experimental value, since Lambert's law was not applied in developing the expression $q/[N(A - 1)]$, Equation 9. Even after making this correction, the value of about 0.95 has been obtained under experimental conditions giving a large experimental error, and the best conclusion we can draw until measurements have been made with a more accurate apparatus is that the ratio of quantum yield to yield per ion pair is probably 1.

At any rate, the results leave little doubt that the secondary chain steps are identical under the two types of radiation, that the alpha particle bombardment also leads to atomic chlorine chains. From the kinetics above, the calculated chain lengths will vary as the square root of the radiation intensity. The photochemical chain length in Table VI is about 5000 molecules per quantum, while an alpha radiation 300 times less in-

TABLE VI

RUN 61. PHOSGENE SYNTHESIS INITIATED BY LIGHT AND BY ALPHA PARTICLES

Time, min., t	Pressures in mm. Total	Phosgene	Pressure, $CO + Cl_2 = P$	$1/P$	$\frac{(1/P_2 - 1/P_1)}{\Delta t}$ ($\times 10^5$)
			Alpha Rate		
(Light off)					
0	715.5	0	715.5	0.0013976	3.0 **(induction**
1	708.0	7.5	700.5	14276	2.6 **period)**
2	701.8	13.7	688.1	14533	4.0
3	692.5	23.0	669.5	14937	3.9
4	684.0	31.5	652.5	15326	4.2
5	675.4	40.1	635.3	15741	4.5
6	666.5	49.0	617.5	16194	5.7
7	656.1	59.4	596.7	16759	
				Average,	4.46
			Light + Alpha Rate		
(Light on)					
7.5	648.3	67.2	581.1	0.0017209	16.5
8.0	635.0	80.5	554.5	18034	17.5
8.5	622.2	93.3	528.9	18907	17.5
9.0	610.5	105.0	505.5	19782	16.8
9.5	600.2	115.3	484.9	20623	19.9
10.0	589.0	126.5	462.5	21622	16.5
10.5	580.5	135.0	445.5	22447	24.4
11.0	569.0	146.5	422.5	23669	16.2
11.5	562.0	153.5	408.5	24480	20.7
12.0	554.5	161.0	393.5	25413	
				Average,	18.4
			Alpha Rate		
(Light off)					
13	547.8	167.7	380.1	0.0026309	5.1
14	544.2	171.3	372.9	26817	5.7
15	540.4	175.1	365.3	27375	6.3
16	536.3	179.2	357.1	28003	5.3
17	533.0	182.5	350.5	28531	6.3
18	529.2	186.3	342.9	29163	4.8
19	526.4	189.1	337.3	29647	5 5
20	523.3	192.2	331.1	30202	7.3
21	519.4	196.1	323.3	30931	
				Average,	5.8

Alpha rate before light measurements, 4.46 **Average,** 5.1
Alpha rate after light measurements. 5.8

Alpha + light rate, 18.4

Subsequent calculation (Table VII) gives (Yield per ion pair)/(Yield per quantum) = 0 78

TABLE VII

PHOSGENE SYNTHESIS

Ratio $M/N:M/h\nu$, i. e., (Yield per ion pair produced)/(Yield per quantum absorbed)

Run	$(1/P_2-1/P_1)$ X 10^5 Light + alpha	Alpha alone	N (= 1.66 X 10^{17} X E_t) X 10^{-14}	q/N[a]	A[b]	$\frac{q^c}{N(A-1)}$ = $M/N:M/h\nu$
..	13.6[d]	6.9[e]	16.6	2.96	3.80	0.78[f]
59	19.4	5.8	5.54	8.94	11.20	0.87
60	17.3	4.4	5.48	9.03	15.40	0.63
61	18.4	5.1	5.25	9.44	13.00	0.78
62	16.0	5.0	5.18	9.55	10.30	1.02
63	18.6	4.8	4.01	12.3	15.00	0.88
65	16.2	3.95	3.89	12.7	16.80	0.81

In the subsequent runs, the sensitivity of the CO + Cl_2 mixture was reduced by admixing small quantities (<10%) of tank oxygen.

Run	$(1/P_2-1/P_1)$ X 10^5 Light + alpha	Alpha alone	N (= 1.66 X 10^{17} X E_t) X 10^{-14}	q/N[a]	A[b]	$\frac{q^c}{N(A-1)}$ = $M/N:M/h\nu$
64	10.4	2.4	3.98	12.4	18.8	0.70
68	5.6	1.19	3.09	16.0	21.0	0.80
66	3.7	0.80	3.68	13.4	21.4	0.66
67	3.85	0.79	3.25	15.2	23.6	0.67
					Average,	0.78

[a] q = Number of quanta absorbed per minute at 760 mm. $P_{CO\,+\,Cl_2}$ = 49.5 × 10^{14}. N = Number of ion pairs produced per minute at 760 mm. $P_{CO\,+\,Cl_2}$. [b] $A = \left[\frac{(1/P_2 - 1/P_1)_{\text{light + alpha}}}{(1/P_2 - 1/P_1)_{\text{alpha alone}}}\right]$. [c] This represents the number of quanta necessary to produce as much reaction as one ion pair. [d] Average of a series of light rates; radon absent. [e] Average of a series of alpha rates; light absent. Calculated from Table II for a radon concentration of 0.01 curie. [f] The value 0.78 obtained from q/NA; see Equation 10.

tense, Table I, Run 42, gives a chain length of over 50,000 molecules per ion pair. The mechanism of the primary step in the alpha particle chain, however, can only be elucidated by further experiments. It probably involves an initial ionization by the alpha particle, while subsequent dissociation gives rise to chlorine atoms which may be produced at the time of ionization or later by collision of the ion with neutral molecules, or upon final neutralization of the ions by recombination; the steps which succeed this atomization mimic those of the photochemical reaction.

Summary

1. The photochemical systhesis of phosgene from carbon monoxide and chlorine has been expressed kinetically by

$$\frac{+dP_{COCl_2}}{dt} = k\sqrt{I_{\text{abs.}} \times P_{CO}} \times P_{Cl_2}$$

If the gas mixture is activated by alpha particle bombardment instead of by light, the reaction obeys this same kinetic equation, i_p, the number of ion pairs produced, being substituted for $I_{\text{abs.}}$, the number of quanta absorbed. This was tested over an eighty-three-fold range of radon concentration and a wide variation of the relative pressures of carbon monoxide and chlorine.

2. Simultaneous measurement of the alpha particle and photochemical reactions shows that the yield per ion pair is equal to the yield per quantum absorbed. This is also true in the presence of oxygen ($<10\%$) which inhibits the reaction.

3. With exceedingly weak radiation, yields as high as 85,000 molecules per ion pair were obtained: the more intense light radiations gave 5000 molecules per quantum absorbed.

4. The secondary steps in the phosgene synthesis involve an atomic chlorine chain mechanism and the above facts prove that this mechanism occurs independently of whether the primary step has been photochemical excitation or ionization by alpha particles.

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THE PHOTOCHEMICAL HYDROGEN–OXYGEN REACTION

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Several attempts have been made to elucidate the kinetics of the interaction of oxygen and hydrogen under influence of light. Andrejew[1] and Coehn and Grote[2] demonstrated the existence of a stationary state in the system water vapor–oxygen and hydrogen, illuminated by the short wave lengths of a mercury arc but did not investigate the details of the reactions involved. Tian[3] succeeded in showing the presence of hydrogen peroxide in illuminated hydrogen–oxygen mixtures and assumed that water is formed only through some intermediary steps involving hydrogen peroxide. Kistiakowsky[4] has shown that while at room temperature the quantum yield of water formation is not far from the value of two, reaction chains are set up in the temperature range where the thermal reaction becomes noticeable, the temperature coefficient of the photochemical water formation not following the Arrhenius equation. Reaction of hydrogen and oxygen photosensitized by mercury vapor has been studied by Marshall[5] and by Bates and Taylor.[6] It has been conclusively demonstrated that water is formed through a secondary decomposition of hydrogen peroxide. Bates and Taylor further noticed that in absence of mercury vapor only ozone is formed, hydrogen peroxide being completely

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[1] Andrejew, J. *Russ. Phys.-Chem. Soc.*, *43*, 1342 (1911).

[2] Coehn and Grote, "Nernst Festschrift," 1912.

[3] Tian, *Compt. rend.*, 152, 1012 (1911).

[4] Kistiakowsky, *Proc. Nat. Acad. Sci.*, *15*, 194 (1929).

[5] Marshall, *J. Phys. Chem.*, 30, 34, 1078 (1926).

[6] Bates and Taylor, THIS JOURNAL, 49, 2438 (1927).

absent. In these latter experiments mainly the mercury line 1842 Å. must have been photochemically active. The present work is concerned with the mechanism of the un-sensitized reaction of oxygen and hydrogen in light of two spectral regions: 1854–1862 Å., by which according to Birge and Sponer,[7] excited oxygen molecules are produced and the region of 1719–1725 Å., which dissociates oxygen molecules in one elementary act, a normal and excited oxygen atom resulting.[8]

The experimental set-up consisted of a condensed spark burning between aluminum electrodes and of a thin-walled quartz vessel of about 100-cc. capacity, through which the reacting gases were passed at measured rates of flow. The reaction vessel was placed at 4-cm. distance from the spark and the space between was filled with streaming air or purified nitrogen. Oxygen in an air layer 4-cm. deep absorbs the strong aluminum spark lines in the neighborhood of 1720 Å. completely[9] while the strong line group 1854–1862 Å. reaches the reaction vessel only very slightly weakened.[9] The correctness of this assumption is proved by the observation that substitution of nitrogen instead of air increased the reaction velocity more than ten-fold. Accordingly, with a layer of nitrogen, more than 90% of the reaction is due to the initial formation of oxygen atoms, while with the air layer only the lines in the band absorption region of oxygen are effective. In order to determine the course of reaction the exit gases were passed through a neutral potassium iodide solution and the liberated iodine was titrated on acidification. This gave the total amount of ozone and hydrogen peroxide formed, since better than 90% of the latter, as established by special experiments, was retained in the wash bottles containing potassium iodide and reacted with it on acidification. Hydrogen peroxide alone was determined colorimetrically with the aid of titanium sulfate solutions. To determine the absolute rate of the reactions involved use was made of the work of Warburg[10] and of Noyes,[11] which shows that the quantum yield of ozone formation in oxygen is, independently of wave length, equal to two. Warburg's experiments indicate further that the yield remains unchanged on dilution of oxygen with nitrogen. Accordingly, in the following experiments the reaction rates in the oxygen–hydrogen mixtures are referred to the rates of ozone formation in similar oxygen–nitrogen mixtures, measured in the same vessel and under identical conditions of illumination. In Pig. 1 are plotted yields of ozone in light of the line group 1854–1862 Å. against the rate of gas flow. Circles refer to a mixture containing 20% O_2 and 80% N_2,

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[7] Birge and Sponer, *Phys. Rev.*, 28, 259 (1926).

[8] Herzberg, Z. *physik. Chem.*, *4B*, 223 (1929).

[9] *Cf.* Lyman, "The Spectroscopy of Extreme Ultraviolet," London, 1928.

[10] Warburg, *Sitzb. Akad. Wiss. Wien*, 216 (1912); 872 (1914).

[11] Vaughan and Noyes, THIS JOURNAL, 52, 559 (1930).

[12] Taylor and Marshall, *Trans. Faraday Soc.*, 21, 560 (1925).

crosses to a mixture containing 80% H_2 instead of nitrogen. Determination of the hydrogen peroxide yield showed that this was formed at a rate of not more than 2×10^{-8} mole per minute (this being the sensitivity limit of the color test as here used) whether the gas flow was 700 or 30 cc./min. In calculating the points in Fig. 1 which were obtained with the highest rates of gas flow, averages have been taken of several experiments made. Since the effect on ozone yield of substitution of hydrogen for nitrogen is of importance for the discussion to follow, Table I presents complete data relating to this point.

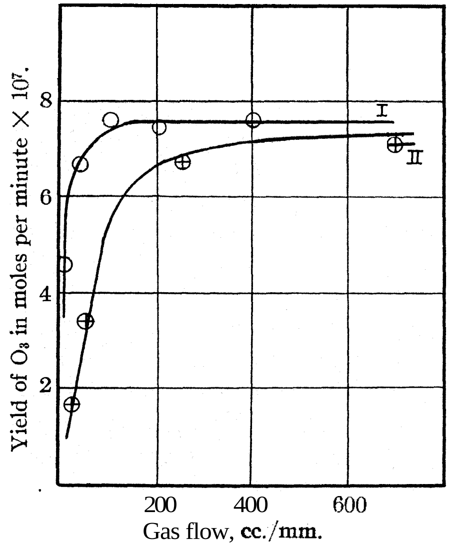

Fig. 1.—Yield of ozone in light of the (mean) wave length 1860 Å. Circles and Curve I, yields in the 1:4 oxygen–nitrogen mixture. Circles and Curve II, yields in the 1:4 oxygen–hydrogen mixture.

Figure 2 presents data obtained with the shorter wave lengths. Circles and Curve I represent ozone yields in the (1:4) oxygen–nitrogen mixture, crosses and Curve 2, ozone plus hydrogen peroxide yields in the (1:4) oxygen–hydrogen mixture, circles and Curve 3, finally, hydrogen peroxide yields alone. All points in Fig. 2 are averages of two or more experiments. The reproducibility of the results in the light of short wave lengths was not as good as in the experiments with the 1852–1864 Å. lines and can be best judged from Pig. 3, in which single experiments have been plotted. In this figure are plotted the relative yields of ozone (represented by circles)

TABLE I

OZONE YIELD

Gas mixture	Rate of gas flow, cc./min.	Ozone yield, moles per minute $\times 10^7$							
20% O_2 + 80% N_2	400	7.62	7.67	7.73	6.60	6.88	6.54	6.60[a]	
20% O_2 + 80% H_2	700	7.62	7.16		5.85	6.88	7.00	6.48	6.88

[a] This second series of determinations has been made with a slightly changed apparatus and was not used in drawing Fig. 1.

and of hydrogen peroxide (crosses) against the composition of the oxygen–hydrogen mixture, the ozone yields in the equivalent oxygen–nitrogen mixtures having been taken for 100%. The ozone yields in mixtures containing hydrogen were obtained by subtracting hydrogen peroxide yields from the total yield as determined by the iodine titration. All these data were obtained with a gas flow of 2000 cc./min. with oxygen–hydrogen and 1500 cc./min. with oxygen–nitrogen mixtures.

Figures 1 and 2 show that with increasing rate of gas flow the yields tend to constant values which represent undoubtedly the maximum yields in absence of secondary photochemical decomposition of either ozone or hydrogen peroxide. In view of all earlier work, it may be further assumed—with a considerable degree of certainty—that the ozone yields, in the oxygen–nitrogen mixtures, are equal to two molecules per quantum of absorbed light energy, irrespective of the wave length. With oxygen–hydrogen mixtures the effect of the two spectral regions is considerably different. While with the 1860 Å. line group practically the same yield of ozone is obtained whether the mixture contain nitrogen or hydrogen, with the short wave lengths and in the presence of hydrogen, the ozone yield is only 25% of that in the presence of nitrogen, but an equal amount of hydrogen peroxide is formed in addition. As Fig. 3 shows, ozone yields in presence of hydrogen are—at least roughly—proportional to the relative concentration of oxygen, whereas the yields of hydrogen peroxide are proportional to the concentration of hydrogen. Since it is well established that in the light of the 1720 Å. spectral region oxygen atoms are primarily formed, one can consider somewhat more in detail their reactions, of which not many are possible.

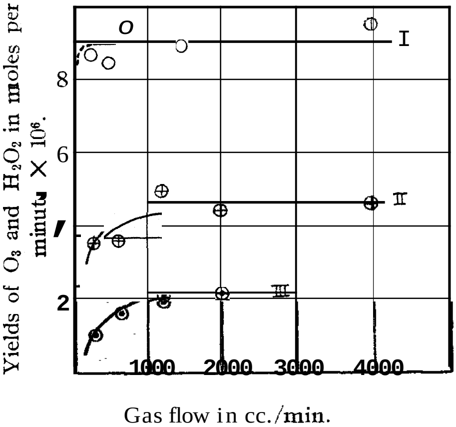

Fig. 2.—Yields of O_3 and H_2O_2 in light of the (mean) wave length 1720 Å. Circles and Curve I, O_3 in the 1:4 oxygen–nitrogen mixture. Crosses and Curve II, O_3 + H_2O_2 in the 1:4 oxygen–hydrogen mixture. Dots and Curve III, H_2O_2 alone in the 1:4 oxygen–hydrogen mixture.

$$O + O_2 + X = O_3 + X \tag{1}$$
$$O + H_2 + X = H_2O + X \tag{2}$$
$$O + H_2 = OH + H \tag{3}$$

X denotes here a molecule of oxygen or hydrogen. These three reactions are in qualitative agreement with the relations observed since they lead to an ozone yield which is proportional to the concentration of oxygen while the rate of the third reaction is proportional to the concentration of hydrogen. In this last reaction hydrogen atoms are produced, but, as was already suggested by Taylor and Marshall[12] and shown by Boehm and Bonhoeffer[13] hydrogen atoms react to form quantitatively hydrogen

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[13] Boehm and Bonhoeffer, Z. *physik. Chem.*, 119, 385 (1926).

peroxide. According to Marshall,[5] or, the average not less than two molecules of this latter are produced by each hydrogen atom. While the first two reactions require three-body collisions and, therefore, should be relatively slow, the third reaction is free from this limitation and, being exothermic, should take place on every collision.[14] That this conclusion is incorrect is shown by the present experiments in which ozone yields equal to or in excess of hydrogen peroxide yields were obtained. Using data here recorded the probability of Reaction **3** can be estimated to 10^{-4} if, as the first approximation, the assumptions are made that all molecular diameters are equal ($\backsim 10^{-8}$ cm.) and that bimolecular collisions occur at atmospheric pressure 1000 times more frequently than termolecular ones (mean free path $\backsim 10^{-5}$ cm.). The only factor which might increase this value is the possibility that the three-body collisions leading to Reactions 1 or 2 occur more frequently than assumed, which means that the molecular effective cross sections are here larger than the kinetic values. The slowness of the reaction of oxygen atoms with hydrogen molecules finds a parallel in a similar reaction of chlorine atoms. By combining Bonhoeffer's[13] data on the reaction H + Cl_2 with calculations made by Trifonoff,[15] one finds that the probability of the reaction Cl + H_2 is somewhat less than 10^{-3} when water vapor is present and is presumably zero in completely dry gases. The hydrogen molecule shows thus a remarkable stability in reactions which should take place on every collision according to the theories of Herzfeld[14] and of others.

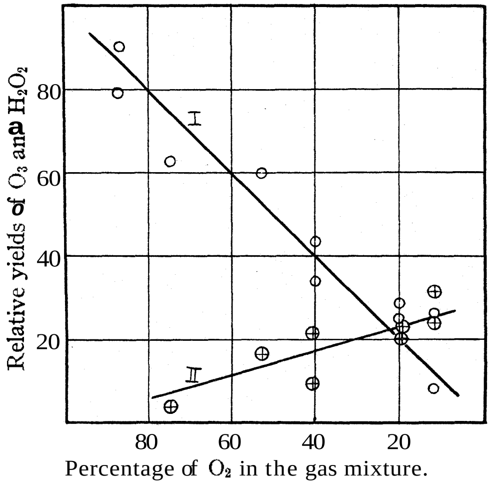

Fig. 3.—Dependence of the yields of O_3 and H_2O_2 on the composition of the gas mixture in light of the wave length 1720 Å. Circles and Curve I, O_3 yields. Crosses and Curve II, H_2O_2 yields.

In the dissociation of the oxygen molecule by light one of the oxygen atoms produced is in the normal ^3P state, whereas the other is, according to Herzberg,[8] in the ^1D metastable state, possessing some 30,000 cal. of excitation energy. The question is of considerable interest whether this difference in the energy levels influences the probability of reaction with hydrogen molecules. No definite answer can be obtained from the experiments with the short wave lengths alone. They can be accounted

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[14] Herzfeld, *Ann. Physik*, 59, 635 (1919).

[15] Trifonoff, *Z. physik. Chem.*, *3B*, 195 (1929).

for by assuming equal probabilities. However, the later discussion will show that the assumption is more helpful that the oxygen atoms in the normal quantum state react with hydrogen molecules more slowly than the excited ones, for which alone the above estimated probability of 10^{-4} would then hold.

The occurrence of Reaction 2 has been so far, left out of consideration. That either this reaction or, and this is less probable, a recombination of oxygen atoms does take place in the hydrogen–oxygen mixture is shown by the observation that there is a deficit in the ozone plus hydrogen peroxide yield as compared with the ozone yield in the oxygen–nitrogen mixtures. Several attempts have now been made to identify water among the primary reaction products by freezing out the products in a liquid-air trap and analyzing the contents on weighing. These attempts failed, due to low yields and the very high gas flow velocities required, but further work under changed conditions is planned. As an indirect proof of the occurrence of Reaction 2 the experiments of Farkas, Goldfinger and Haber[16] may be considered. They succeeded in exploding $O_2 + H_2$ mixtures by introducing oxygen atoms in fairly high concentration. Formation of either ozone or hydrogen peroxide is not exothermic enough to cause explosion and a strongly exothermic reaction of the type represented by Reaction 2, eventually leading to short chains, must have occurred in these experiments.

It remains now to consider results obtained with the 1860 Å. spectral region. These experiments are not quite in accord with the data already discussed. The essence of the results obtained is that with the long wave lengths practically no reaction occurs between hydrogen and oxygen, ozone being quantitatively formed. If the secondary process on excitation of an oxygen molecule is its dissociation into atoms on collision—there is enough energy for the process—this result would be quite incomprehensible. The other possible process is

$$O_2 + O_2 = O_3 + O \tag{4}$$

the oxygen atom reacting then by 1, 2 or 3. But this scheme also requires a lower ozone yield and formation of hydrogen peroxide in presence of hydrogen even if the excited oxygen molecules do not react with hydrogen at all. In the 1:4 oxygen–hydrogen mixture one would expect (see Fig. 2) at most $50 + 25/2 = 62\%$ of ozone and at least $25/2 = 12\%$ of hydrogen peroxide as compared with the ozone yield in a similar oxygen–nitrogen mixture. The experiments show (Table I) that the sum of ozone and hydrogen peroxide formed is about 97–99%, while the hydrogen peroxide yield does not exceed 3%. This latter observation is, incidentally, in complete accord with the earlier mentioned results of Bates and Taylor. The difficulty in connection with the hydrogen peroxide yield is removed

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[16] Farkas, Goldfinger and Haber, *Naturwissenschaften*, 17, 674 (1929).

if the suggestion be accepted that the probability of Reaction 3, which was calculated to 10^{-4} for excited atoms, is smaller in case of normal oxygen atoms, such as are produced in Reaction 4. But even with this assumption the excess of ozone yield over that calculated remains unexplained, since there are no reasons to assume that with normal oxygen atoms the ratio of the reaction velocities 1 and 2 is different than in case of excited atoms. This question, therefore, must be left open at present but it is hoped that further experiments now under way may bring a solution of this problem.

Summary

1. The oxygen–hydrogen reaction has been studied in light of the two spectral regions 1719–172.5 Å. and 1854–1862 Å.

2. The effect of these spectral regions is markedly different. While the longer wave lengths produce only ozone in an amount equal to that produced in similar oxygen–nitrogen mixtures, in light of shorter wave lengths the yields of ozone in the presence of hydrogen are smaller but hydrogen peroxide is formed in addition.

3. The probable reaction mechanism has been discussed. The probability of the reaction $O + H_2 = OH + H$ has been estimated to 10^{-4}, a much smaller value than that predicted theoretically.

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THE VAPOR PRESSURE AND HEATS OF FUSION AND VAPORIZATION OF FORMIC ACID

BY ALBERT SPRAGUE COOLIDGE

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Introduction

In a recent paper[1] were given data on the density of formic acid vapor, together with some isolated vapor pressure data obtained in studying the process of purification. These data were obtained in order to make possible use of the Clapeyron equation in calculating heats of adsorption from equilibrium pressure data. The same equation should, of course, give the heats of evaporation of pure solid or liquid formic acid, when the corresponding vapor pressures are introduced. The case is interesting because of the wide deviation of the vapor from the perfect gas laws, produced by association. The only calorimetrically determined quantities by which the Clapeyron equation could be checked appeared to be the heat of vaporization of the boiling liquid, and the heat of fusion of the solid, which can be compared with the difference between the vaporization heats calculated for the solid and liquid at the triple point. Using

[1] Coolidge, THIS JOURNAL, 50, 2166 (1928).

the values of the vapor pressures from "International Critical Tables," it was found that in neither case did the calculated and observed values agree. It seemed worth while, therefore, to redetermine both vapor pressures and latent heats with the very pure formic acid available, in the hope of getting a thermodynamically consistent set of data.

Since the observed heat effects are to be compared with values computed by a process involving temperature differentiation of the observed pressures, it is clear that a higher order of accuracy is needed in measuring the latter than the former. Therefore, no attempt was made to surpass a precision of, say, 0.5% in the calorimetry, while no effort was spared to perfect the thermometry and manometry, and it is believed that the error does not exceed 0.1%.

Instability of Formic Acid

It was necessary to take constant precautions against errors arising from the spontaneous decomposition of the acid into water and carbon monoxide. This reaction appears to occur in the liquid at all temperatures, and to cease only when the acid is frozen. However, at room temperature the evolution of permanent gas is very slow, and does not interfere with the measurements provided the sample is one which has been pumped free from gas while frozen, and has been melted just before the experiment. At temperatures approaching 100° decomposition is more rapid, and cannot be ignored. In one experiment, a quantity of liquid, carefully freed from gas, was confined by a column of mercury of about 30-cm. height in addition to the atmospheric pressure, and was then raised to 100°. Within five minutes bubbles begain to escape through the mercury, Since the pure acid boils at 100.5°, the bubbles must have contained considerable permanent gas. Again, it was observed that when the pure acid was gently boiled under a reflux condenser, protected from atmospheric moisture, the boiling point rose a degree in ten hours, due presumably to dilution of the acid by the water resulting from its decomposition. The heat of combustion[2] of the acid is 62,800 calories per formula weight; that of carbon monoxide is 68,100 calories; the decomposition is, therefore, endothermic,a bsorbing 5300 calories per formula weight.

Vapor Pressure Measurenients

For temperatures up to 80° a static method was used to determine the vapor pressures. The acid was placed in a bulb communicating with a manometer on which pressures could be read to 0.01 mm. as high as 100 mm. For higher pressures, this instrument was used to determine the difference in pressure between the bulb and the rest of the system, in which a pressure of air nearly equal to that in the bulb was established, and could be read off another manometer by means of a cathetometer.

The bulb was maintained at the desired temperature, while the connections and

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[2] "International Critical Tables," Vol. V, p. 165.

manometer must, of course, be kept slightly warmer to prevent distillation. A temperature of about −5° was obtained with a sodium chromate eutectic. The salt, a c. P. product, was not further purified, and the exact temperature obtained was not always the same; in any one experiment, however, the temperature, as shown by two thermometers in different positions, was uniform and constant to 0.01". Other temperatures up to 20° were secured with ice- and water-baths. From 30 to 80° an oil-bath was used. It was contained in a Dewar vessel which, together with the manometer and connecting tubing, was mounted in an air-bath with a plate-glass front. The air was maintained a degree or two hotter than the oil, which was prevented from overheating by a very slow stream of water through a coil. The temperature of mercury in manometer and exposed thread of thermometer was thus controlled, and suitable reductions applied.

The main supply of acid used had been purified in the manner described in the previous paper until it had the same vapor pressure at 0°, and was, therefore, probably 99.99% pure. It was kept continuously frozen to prevent deterioration. Samples for the measurements were distilled into the bulb, and before each reading were gently pumped to remove possible traces of permanent gas. At 70 and 80" constant readings were not obtained, the pressure rising steadily after each pumping, without approaching any limit. This situation was met by increasing the size of the dead space so as to dilute the evolved gas, and by making readings at definite time intervals after each pumping. By extrapolating back to zero time, satisfactory values could be obtained.

To extend the range upward, boiling points were taken at atmospheric pressure, and also at about 1000 mm. In this method no error can be produced by accumulation of carbon monoxide, since this gas is swept away by the stream of fresh vapor rising from the liquid. In order to minimize the error due to dilution with water, the boiling was reduced to the shortest possible time, and the acid was once repurified between readings. Nevertheless, it is possible that the values found may be a few hundredths of a degree too high.

Temperatures of 20° and higher were read on a thermometer certified by the Bureau of Standards. Particular care was taken with the temperatures below 20°, on which the calculation of the heat of fusion depends. The thermometer had been certified at ten degree intervals, but the correction at 10° was so different from that at either 0 or 20° that interpolation seemed uncertain. Therefore, the scale used below 20° was the mean of five good thermometers, including that certified by the Bureau of Standards and one certified by the Reichsanstalt, which were all carefully compared between −5 and 20". It is unlikely that the error exceeds 0.02°.

The triple point of formic acid is 8.25°, but the liquid can be cooled to −5° without immediate solidification; attempts to go below −5° always froze the acid. In attempting to measure the sublimation pressure, it was found that when a sample of acid having the correct vapor pressure as liquid at 0° was simply frozen and gently pumped, a pressure of about 8.7 mm. was obtained at 0°. The value given in the first paper was 8.67 mm. However, on exhaustive pumping, accompanied by occasional fusion and resolidification, the pressure dropped to 8.22 mm., below which it failed to go even when almost all of the sample had been pumped away. Evidently traces of volatile matter which remain in solution in the liquid without perceptible effect upon the vapor pressure, are set free on crystallization, and can be removed only with difficulty. The vapor pressure of the solid thus prepared was also determined at −5°. The pressure was also determined over a mixture of solid and liquid, at a temperature of 8.28" (8.26° was given in the first paper). Attempts were made to detect changes in the triple point due to variations in the conditions under which the crystals were formed, or their age, but no variation was found.

TABLE I

VAPOR PRESSURE MEASUREMENTS (MILLIMETERS OF MERCURY)

Liquid		Liquid		Solid	
T	*P*	*T*	*P*	*T*	*P*
−5.23°	8.12	49.93	130.1	−5.07°	4.98
0.00	11.16	59.98	192.7	0.00	8.22
8.25	17.94	70.04	280.6	8.25	17.94
12.57	22.72	79.93	395.6		
20.00	33.55	100.68	762.5		
29.96	54.36	110.62	1017.6		
39.89	85.18				

Table I gives the experimental values for the vapor pressure of solid and liquid, including the boiling points. Each entry is the mean of three closely concordant measurements, except those for the solid at −5° (two measurements) and for the liquid at 60, 80 and 110° (one measurement each).

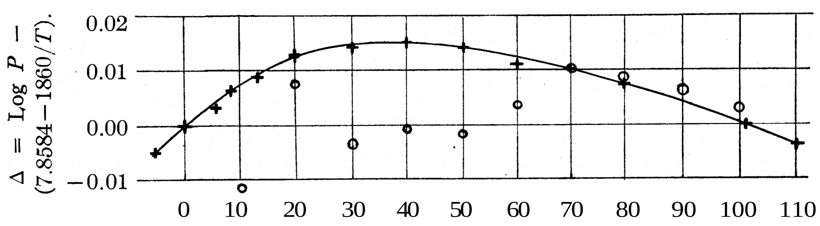

Fig. 1.—Vapor pressure of the liquid (deviation plot).

Adjustment and Comparison of Data

The three values for the vapor pressure of the solid are represented, to within 0.01 mm., by the equation

$$\text{Log P} = 12.486 - 3160/T \tag{1}$$

in which log P is the common logarithm of the pressure in mm., and T is the absolute temperature reckoned from −273.1°C. They may be compared with the values in "International Critical Tables."[3] These values are given only at temperatures from 1 to 8°, but may be easily extrapolated to 0 and 8.25°. The result is

Temperature	0°	8.25°
I. C. T.	8.0	18.0
A. S. C.	8.22	17.94

The experimental values for the vapor pressure of the liquid may be approximately represented by the equation

$$\text{Log P} = 7.8584 - 1860/T \tag{2}$$

but the deviations are systematic. Figure 1 shows the deviation plot, the quantity $\Delta = \log P - (7.8584 - 1860/T)$ being plotted against the

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[3] "International Critical Tables," Vol. III, p. 209.

temperature. The present data are represented by crosses, those of the "International Critical Tables"[4] by circles. A smooth curve can be drawn through the crosses so that none of them, except the single determination at 60°, falls more than 0.0005 from the curve. This corresponds to a discrepancy of 0.12%. By taking A from this curve at round temperatures, values of the vapor pressure can be accurately interpolated. The results are given in Table II, which also shows the "International Critical Tables" values. The values at 0 and 20° are in excellent agreement with the corresponding values published in my first paper; that at 10° is a trifle lower (19.76 instead of 19.88) and is doubtless more reliable. The table also shows the apparent molecular weight of the saturated vapor, calculated as explained in the first paper.

TABLE II

INTERPOLATED VAPOR PRESSURES (MILLIMETERS OF MERCURY)

	Liquid			Solid		
T	$P_{\text{A. S. C.}}$	$P_{\text{I. C. T.}}$	M	$P_{\text{A. S. C.}}$	$P_{\text{I. C. T.}}$	M
0°	11.16	...	85.51	8.22	[8.0]	84.45
8.25	17.94	...	84.57.	17.94	[18.0]	84.57
10	19.76	18 9	84.37			
20	33.52	33.1	83.15			
30	54.55	52.2	81.88			
40	85.59	82.6	80.57			
50	130.4	125.9	79.24			
60	193.4	189.7	77.90			
70	280 2	279.6	76.56			
80	396.4	398.1	75.22			
90	549.4	552 1	73 90			
100	747.6	753.4	72.60			
100.5	...	760.0	...			
100.57	760.0	...	72.55			
110	1000	...	71.33			

Latent Heat Measurements

The latent heats directly measured were the heat of fusion at the triple point and the heat of vaporization of the liquid at temperatures from 0 to 100°.

For the former, a very simple calorimeter was used, consisting of a Dewar cylinder holding 200 cc. of water, provided with a stirrer, a Beckmann thermometer, and a heater of 44.5 ohms resistance, made of wire of negligible temperature resistance coefficient, and enclosed in a copper envelope. Current was supplied at 15 volts, being controlled by a sensitive voltmeter which could be read to 0.01 volt, and which was found actually correct to that degree by potentiometric comparison with a standard cell. The room temperature was constant within 0.5°, and it was found that

[4] "International Critical Tables," Vol. III, p. 215.

when the calorimeter was at room temperature, and evaporation stopped by a layer of kerosene, no detectable heat exchange occurred within twice the time required for a determination. During an experiment the calorimeter temperature fell for a few minutes to some 2° below that of the room. The rate of leak at that head was determined and the appropriate correction applied; it amounted to about 0.5% of the total heat measured.

The scheme of measurement consisted of introducing frozen acid into the calorimeter, and determining the time of current flow required to reestablish the original temperature. The acid (about 8 g.) was sealed into a vessel with five fingers, which it partially filled, thus offering a larger surface for heat transfer than a plain bulb. After freezing, it was left for some time in water at 7°, and was then quickly transferred, with a hasty wiping, to the calorimeter. The method seemed at first unpromisingly crude, but experiment showed that the errors due to the carrying over of cold water and to absorption of heat in transfer were surprisingly constant. At the same time the current was turned on and allowed to flow for a time which preliminary trial showed would nearly restore the original temperature. When equilibrium had been established, the temperature was found a few hundredths of a degree too low; the time of current flow which would have been needed to make good the deficiency was readily estimated. For example, in one experiment, the current flowed for 8.25 minutes, and the final temperature was 0.045' too low. If no thermal leak had occurred, it would have been 0.055° too low. Since 3.8 minutes of current were needed to raise the calorimeter 1° (when the acid was already at the calorimeter temperature) the extra current needed to restore exactly the original temperature would be 0.21 minutes, making the total time 8.46 minutes. Other determinations gave 8.40, 8.46 and 8.44 minutes, the average being 8.44. In some cases the acid was freshly frozen, in others it had been frozen for some hours.

What was actually measured was, of course, the heat of fusion at the triple point, plus the heat content of the solid from 7 to 8.25°, plus the heat content of the liquid from 8.25' to the calorimeter temperature, plus the heat content of the glass over the whole range, plus the errors of transfer. Exactly similar experiments were made (alternately with those described) in which the only difference was that the acid was not frozen. The results were 1.31, 1.34 and 1.31 minutes, average 1.32. The sum of heat quantities measured is evidently the same as before, except that the heat of fusion is absent, and the liquid, instead of the solid, has been heated from 7 to 8.25°. The difference between the two results, 7.12 minutes, evidently represents the heat of fusion at 7°. Similar determinations in which the original temperature was 0° gave 6.94 minutes, corresponding to the heat of fusion at 0°. The extrapolated value at 8.25° is 7.15 minutes, with a probable error of 0.03.

These values are given first in minutes, rather than in joules per gram, because an unfortunate accident prevented the exact determination of the quantity of acid used, and no more pure acid was available for a repetition. The vessel and contained acid were weighed, but when the vessel was opened to remove the acid, the liquid was thrown forcibly back by the inrush of air, and one of the fingers was broken. Almost all of the fragments were recovered and weighed, and by piecing them together it was estimated that not over 0.05 g. of glass was lost. On this basis, the acid weighed 7.85 grams. If, in reality, more glass was lost, the true weight of the acid was less, the true heat of fusion higher than that calculated, namely 268 joules per gram at 0°, 275 joules at 7° and 276 joules at 8.25°. The value given in "International Critical Tables"[5] is 246.5 joules.

The temperature coefficient indicates that the liquid has, as usual, a higher specific heat than the solid. Indeed, this difference can be taken directly from the experimental data, and amounts to 1 joule per degree per gram; this figure, involving differences between four larger quantities, is subject to a large uncertainty, estimated at ±0.2. According to "International Critical Tables" the specific heat of the liquid is 1.83 joules[6] and that of the solid 1.80 joules.[7] The latter datum, as well as those in Landolt–Börnstein,[8] is based on a paper by Massol and Faucon,[9] an inspection of which reveals that it was lauric acid, and not formic acid, with which they were obtained. There appears to be no reliable determination of the heat capacity of crystalline formic acid. Massol and Guillot[10] state that they found the specific heat of the solid to exceed that of the liquid, but as they make the same statement about acetic acid, which is certainly wrong, their figures must be considered worthless.

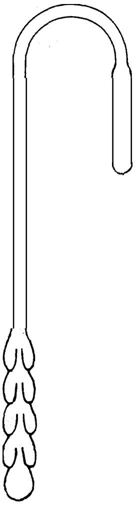

Fig. 2.—Device for ice calorimetry of heat of vaporization.

The heat of evaporation of the liquid at 0° was obtained by allowing a known quantity to evaporate slowly out of an ice calorimeter. The acid was sealed into a device illustrated in Fig. 2. The technique used in measuring and transferring the acid to this device was the same as that which had been used in filling the globes in which the vapor density had

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[5] "International Critical Tables," Vol. V, p. **132.**

[6] *Ibid.*, Vol. V, p. 107.

[7] **Ibid.**, Vol. V, p. 101.

[8] Landolt–Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Vol. II, p. 1266.

[9] Massol and Faucon, *Compt.* rend., 153, 268 (1911) (not Vol. 154 as quoted in I. C. T.).

[10] Massol and Guillot, *ibid.*, 121, 208 (1895).

been determined. The lower bulb contained a series of traps designed to hold the acid in several pools, in order to distribute the absorption of heat along the length of the calorimeter tube. In use, the acid was all collected in the lower tube, which was then inserted in the calorimeter. When equilibrium was established, the upper tube was cooled to about $-3°$, causing the acid to distil over in from one to two hours. Trials with water had showed that this procedure gave values correct within 1 In order to avoid errors in measurement and transfer, two samples of acid were used.

In determining the heats of vaporization at higher temperatures, it seemed important to use a condensation method, instead of the usual scheme in which the energy required to boil away a certain quantity of liquid is determined. For in the usual method decomposition is to be feared, especially if the boiling is produced by a hot platinum wire, and the heat absorbed by decomposition will be added to the true heat of vaporization, producing a positive error. A method was, therefore, devised in which a known amount of cold mercury was introduced into a bulb which was bathed in the saturated vapor, and the quantity of condensed liquid measured by volume. Figure 3 is a sketch of the apparatus. The vapor rises from liquid acid boiling in the bulb B, and is condensed by a reflux condenser attached at C. The pear P is heated by the vapor to the boiling point, and the condensate drips off into the calibrated tube T, where its level is read by a cathetometer. The pear is shielded from liquid running down from the condenser by the umbrella U. The rod R serves to carry the condenser liquid to the stem of the umbrella without splashing; it then runs over the surface and down the rods attached to the pointed tips, finally dropping off from the goose-neck bends just below the opening of T. It was found that when the pear had once been brought to the boiling point, no change in level in T occurred, showing that the shielding was adequate. The apparatus was constructed with a ground joint at G, but this joint was never opened in use, but was kept sealed with mercury. The acid was introduced or withdrawn by distillation through the top of the condenser, which was sealed to the main purifying and storage apparatus. Provision was made for admitting dry air at atmospheric pressure, or at a pressure controlled by a manostat.

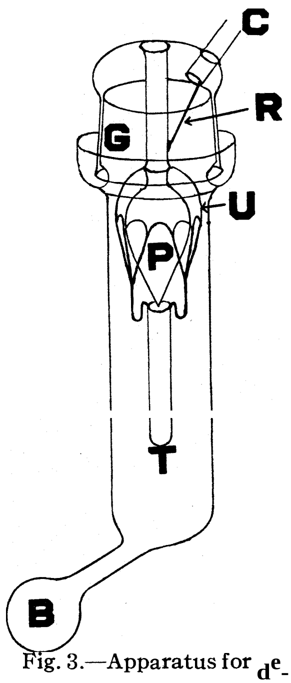

Fig. 3.—Apparatus for determining heat of vaporization.

Mercury from a water-jacketed pipet was then suddenly injected into P. The pipet was provided with *a* nozzle through which the mercury was forced by compressed air, the stream being so directed as not to touch the walls of the stem. As the nozzle was bathed in the water of the jacket, the only opportunity for the mercury to absorb heat prematurely was from the warm air in the stem, and the quantity so absorbed during the five or six seconds required to empty the pipet must have been very small. An obvious improvement would have been to evacuate the pear and its stem. When the level of liquid in T had again become constant, it was read, and the exact temperature of the mercury in P taken by introducing a thermometer. The weight of acid was calculated from the known volume of the tube, with the aid of the expansion formulas of Pierre and of Zander,[11] which agree sufficiently for the purpose.

A specimen calculation is as follows

Weight of mercury	268 g.
Original temperature	10 4°
Final (boiling) temp.	42.2"
Heat absorbed by mercury	282.8 cal.
Original height in T	830.6 mm.
Final height	859 8 mm.
Corresponding volume	2 23 cc.
Density of acid at 42.2°	1.195
Weight condensed	2.666 g.
Heat of evap. per gram	106.0 cal.

In working at atmospheric pressure, a serious difficulty arose. The liquid collected in the tube T, being maintained at about 100°, began to decompose spontaneously, with escape of bubbles. This interfered with reading the level of the liquid, not only because of uncertainty as to the volume occupied by the bubbles, but because they carried away considerable acid, causing the level to fall rather rapidly. (It was at first thought that this phenomenon was caused by insufficient purification of the acid, causing a fractionation to occur, in which the more volatile fraction collected in the tube, and was actually boiled away by immersion in the hotter vapor from the less volatile residue, but repeated purification caused no diminution in the rate at which the bubbles evolved. The experiment with acid confined under mercury was then carried out in order to prove actual decomposition.) No way was found to avoid this difficulty, and the readings made at this temperature had to be corrected by admittedly uncertain estimates. They are, therefore, not as reliable as the others.

Table III contains the results of the directly determined heats of vaporization, together with the value given in "International Critical Tables."[12]

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[11] Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Vol. II, p. 1233.

[12] "International Critical Tables," Vol. V, p. 136.

TABLE 111

MEASURED HEATS OF VAPORIZATION OF THE LIQUID

	0°	42.2°	64.5°	100.5°
Observed, cal. per g.	110.6 102.4 103.0	106.0 105.9 106.6	109.3 109.4 109.4	115.5 115.4
Average	102.7	106.2	109.4	115.5
Joules	430	445	458	483
"I. C. T."	. .	...	...	502

Application of the Clapeyron Equation

The heat of vaporization per gram, λ, should be given by the equation

$$\lambda = T\Delta v(\mathrm{d}P/\mathrm{d}T) \qquad (3)$$

Here Av is essentially the volume of one gram of saturated vapor, hence we may write

$$\Delta v = (1 - \eta)RT/MP \qquad (4)$$

where M is the apparent molecular weight at the particular pressure and temperature considered, and η is the ratio of the vapor density to that of the liquid, and constitutes a correction term which is negligible except at pressures approaching the atmospheric. The Clapeyron equation, therefore, takes the form

$$\lambda = -\frac{R\,\mathrm{d}\ln P}{M\,\mathrm{d}(1/T)}(1 - \eta) = -19.146\,\frac{\mathrm{d}\log P}{M\,\mathrm{d}(1/T)}(1 - \eta) \text{ joules per gram} \qquad (5)$$

It follows from Equation 1 that the value of d log $P/\mathrm{d}(1/T)$ for the solid is —3160. At the triple point M has the value 84.57 and η is negligible. The calculated heat of sublimation is, therefore, 716 joules per gram.

For the liquid, we have evidently

$$\mathrm{d}\log P/\mathrm{d}(1/T) = -1860 - T^2\,\mathrm{d}\Delta/\mathrm{d}T \qquad (6)$$

A being the deviation function plotted in Fig. 1. The coefficient can be read off the smooth curve. For the four temperatures at which direct measurements were made, the calculated heats of vaporization are as shown in Table IV.

TABLE IV

APPLICATION OF CLAPEYRON EQUATION

Temp., °C	0°	42.2°	64.5°	100.5'
$\mathrm{d}\Delta/\mathrm{d}T \times 10^4$.	9	−1	−2	−3.5
d log $P/\mathrm{d}(1/T)$	−1927	−1850	−1837	−1811
M..	85.51	80.28	77.30	72.55
$\eta \times 10^4$	....	....	7	20
λ, calcd.	432	441	455	477
λ, obs..............	430	445	458	483

The calculated heat of vaporization of the liquid at the triple point is 434 joules, that of the solid 716 joules, and therefore, by subtraction, the calculated heat of fusion is 282 joules; the observed value was 276, or perhaps a trifle higher. We may also calculate the heat of fusion at 0°, but the method is less simple, because in this case the vapor produced by the liquid is at a different pressure from that produced by the solid, and the joule heat has to be considered. Let H_s be the heat content of one gram of solid, and H_8 that of its saturated vapor, while H_f and H_{11} are the corresponding quantities for the liquid and its vapor. Then we wish to calculate $H_f - H_s$ (neglecting the fact that these quantities refer to slightly different pressures). We have calculated that $H_{11} - H_f$ is 432 joules at 0°, and $H_8 - H_s$ comes out 717 joules. We need to know

$$H_{11} - H_8 = \int_{8.22}^{11.16} \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}P \tag{7}$$

Now

$$(\partial H/\partial P)_T = v - T(\partial v/\partial T)_P = \left(\frac{\partial(v/T)}{\partial(1/T)}\right)_P = \frac{R}{P}\left(\frac{\partial(1/M)}{\partial(1/T)}\right)_P \tag{8}$$

and the last differential coefficient can be evaluated from the dissociation equations for the vapor, namely

$$\frac{P \times (92 - M)^2}{46(M - 46)} = K \tag{9}$$

$$\text{Log } K = 10.758 - 3092/T \tag{10}$$

(These equations are taken from the first paper. The constants of the second equation have been slightly altered in order that T may be calculated from an absolute zero of −273.1°C., instead of −273°, the round number having been used in the first paper. Through an error, the value of K at 70° is there given as 56.60; it should be 55.72.) Logarithmic differentiation of (9) gives

$$\frac{M^3}{(92 - M)(M - 46)} \times \left(\frac{\partial(1/M)}{\partial(1/T)}\right)_P = \frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = -7120 \tag{11}$$

The average value of M at 0° between 8 and 11-mm. may be taken approximately as 85, and, therefore, over a small range in that vicinity, we may take $\partial(1/M)/\partial(1/T)$ as constant and equal to —3.2. Substituting in (8) and then in (7)

$$H_{11} - H_8 = -23.R \int_{8.22}^{11.16} \mathrm{d}\ln P = -8.1 \text{ joules per gram} \tag{12}$$

The calculated heat of fusion at 0° is, therefore, 717—432—8 = 277 joules, 5 joules less than at the triple point. This makes the specific heat of the liquid greater than that of the solid by 0.6 joule, a figure considerably lower than the 1 ± 0.2 given by direct measurement. .

Criticism and Discussion

It will be seen that the present data are thermodynamically consistent to as good an approximation as is ordinarily obtainable in such calculations. The vapor density data were found by Ramsperger and Porter[13] to be in complete agreement with their own. The vapor pressure data, while

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[13] Ramsperger and Porter, THIS JOURNAL, 50, 3036 (1928).

more regular than those of the "International Critical Tables," are not greatly different, but the directly determined heats of fusion and vaporization, if correct, require a considerable revision of the accepted values. In their favor stands the fact that they are thermodynamically consistent with the vapor density and pressure data, while the values in "International Critical Tables" are not. It is to be noted that the "International Critical Tables" value for the heat of vaporization is based upon the work of three authors, of whom one[14] worked long ago, while the other two[15] used a platinum wire to boil the acid, which may have caused error through decomposition. Neither author mentions any special precautions observed with the acid, which was merely one of several substances investigated. As for the heat of fusion, Pettersson[16] worked at a low temperature, and by a method which is stated by "International Critical Tables" to give low results. The paper of Guillot[17] is not available, but in view of his statement about the specific heat of crystalline acetic acid,[10] it seems more than likely that his results were vitiated by premelting, causing the specific heat of the solid to appear too great and the heat of fusion too low. The present evaluation of the difference in the specific heats of the solid and liquid must be regarded as giving an orientating value only, but leaves little doubt that it is of the ordinary sign and magnitude.

Interpretation

In the case of a solid or liquid emitting a vapor of constant molecular weight, a plot of log P as ordinate against $1/T$ as abscissa yields a curve whose slope is at every point proportional to the heat of vaporization. The temperature coefficient of the latter depends on the difference between the coefficients $\partial H/\partial T$ for the two phases, evaluated under the restriction that the pressure shall be maintained equal to the saturation pressure. For substances which may be regarded as perfect gases or incompressible dense phases, these coefficients are equal to the specific heats at constant pressure. For solids, C_p is nearly equal to C_p of the vapor, so that the temperature coefficient is small and the vapor pressure curve is approximately straight. Liquids have higher C_p, causing their heat of evaporation to decrease with rising temperature, and the vapor pressure curves to be concave downward. The heat of vaporization of liquid formic acid has been shown to rise rapidly with the temperature, and this is due to the very high value of $\partial H/\partial T$ for the vapor. There is no simple exact interpretation of $\partial H/\partial T$, but its largest term is the heat absorbed when the temperature of the vapor is raised under the prescribed conditions; and this is abnormally great with formic acid be-

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[14] Favre and Silbermann, *Compt. rend.*, 23, 413 (1846).

[15] Marshall, *Phil. Mag.*, 43, 29 (1897); Brown, *J. Chem. Soc.*, 83, 987 (1903).

[16] Pettersson, *J. prakt. Chem.*, 24, 129, 293 (1881).

[17] Guillot, "Thèse," École Pharm., Montpellier, 1895.

cause the heating produces dissociation of double into single molecules with great absorption of energy.

A simple calculation will show to what extent the abnormal temperature coefficient may be accounted for by this interpretation. We may conceive of evaporation as a stepwise process, in which double molecules of vapor are first produced by evaporation, after which a certain fraction of them dissociate, absorbing heat at the rate of 14,125 calories per mole (value given in first paper) or 645 joules per gram. The whole process is conceived as isopiestic. Now, at 0°, only 7.6% of the saturated vapor is dissociated, so that, when 1 gram evaporates, 49 joules can be referred to dissociation. At 100° the figures are 30% and 194 joules, so that we might expect the heat of vaporization to be 145 joules higher at 100° than at 0°. Actually, it is only about 50 joules greater, because, superposed on the increase caused by dissociation in the vapor, we have also the normal decrease characteristic of all liquids. By adding to the actual heats of vaporization the calculated heats required to complete the dissociation of the vapor into single molecules, we may determine the heat of evaporation of single molecules from the actual liquid. The same result may be obtained by calculating the partial pressure of single molecules in the saturated vapor at various temperatures and applying the Clapeyron equation. Expressing the result in joules per mole (46 g.), we obtain 47,200 at 0° and 42,800 at 100°, a decrease of 4400. It is interesting to compare these figures with those for water, which in the liquid state is in many ways similar to formic acid, but which produces a monomolecular vapor on evaporation. For water, the heat of vaporization is 44,900 joules per mole at 0° and 40,700 at 100°, a decrease of 4200. The similarity in the figures is striking, and shows clearly how the actual temperature coefficient for formic acid is compounded of a positive term due to molecular association in the vapor, and the normal negative term. The latter may be interpreted as due to the excess of C_p for the liquid over the C_p which the vapor would possess if the equilibrium were frozen.

Although the latent heat increases with temperature, the vapor pressure curve is markedly concave downward. This is, of course, due to the variability of M in the Clapeyron equation. An inspection of Equation 5 together with Table IV shows that in determining the value of $d \ln P/d(1/T)$ at increasing temperatures, the decrease in M outweighs the increase in λ.

The vapor pressure curve of the solid presents an interesting case. Let us write Equation 9 in the form

$$P \times \varphi(M) = K$$

where $\varphi(M)$ is a function of M alone. Now, taking the value of K from Equation 10 and that of P from Equation 1, we see that they have nearly the same temperature coefficient, so that M is nearly independent of temperature. As a result the curve will be of the same type obtained with other solids, and will be almost straight. The specific heat of the saturated vapor will contain only a small term due to association. This small term is of opposite sign to that which occurs in the case of the liquid, for the saturated vapor of the solid undergoes a slight increase in association when heated, due to the very rapid rise in pressure. Assuming C_p for the solid equal to C_p for the vapor with frozen equilibrium, we shall have a slight fall in the heat of sublimation with rising temperature.

While the heat of sublimation probably falls, and the heat of evaporation rises with the temperature, the heat of fusion rises, instead of falling, as it must do if it were, as in the ordinary case, the difference between the other two. We have seen already that this is due to the presence of a term $H_{11} - H_8$, which is usually zero. This term may also be interpreted as due to variation in the degree of dissociation. Thus, at 0° the liquid produces a vapor 7.6% dissociated; the vapor from the solid is 9.1%, and conversion of one into the other involves some 9 joules of dissociation heat. (The thermodynamic evaluation gave 8 joules.)

Summary

The vapor pressure of pure formic acid, both solid and liquid, has been carefully determined between -5 and 110°.

The heat of vaporization of the liquid, and the heat of fusion of the solid, have been determined with moderate accuracy at several temperatures.

The values so found are thermodynamically consistent among themselves, but differ, sometimes considerably, from previously accepted values.

It is shown that the differences in thermal behavior between formic acid and substances producing normal vapors, especially water, are just those to be expected when account is taken of the heat absorbed or supplied by shifting of the dissociative equilibrium in the vapor.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE DETERMINATION OF CALCIUM BY IGNITION OF CALCIUM OXALATE TO CARBONATE IN AIR

BY H. H. WILLARD AND A. W. BOLDYREFF

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Introduction

Because of its practical importance the quantitative determination of calcium has received a great deal of attention, and the various methods described in the literature have been made the subject of exhaustive critical study. Winkler[1] has tested and reviewed a number of methods, recommending, as the most reliable, precipitation as oxalate followed by ignition to oxide. Szebelledy,[2] continuing Winkler's work, recommends drying the precipitated oxalate to $CaC_2O_4 \cdot H_2O$. Ewe[3] compared experimentally ten standard methods, and determined their relative merits.

It is obvious that by using the proper temperature precipitated calcium oxalate, theoretically at least, can be changed quantitatively into any of the following forms: $CaC_2O_4 \cdot H_2O$, CaC_2O_4, $CaCO_3$ or CaO.

Weighing as $CaC_2O_4 \cdot H_2O$ always involves the danger of a slight variation in the water content; weighing as CaC_2O_4 is objectionable because of its hygroscopicity, and the errors in weighing CaO are too well known to need mentioning.

In spite of its advantages, the ignition of calcium oxalate to carbonate in air has never been satisfactorily studied. The proper temperature range has never been accurately determined, and the conditions given are usually such that the precipitate is partly converted to oxide, which must then be changed to carbonate by treating it with ammonium carbonate and igniting gently. This method was originally proposed by Fresenius[4] and studied by Irby,[5] Fram,[6] Brunck[7] and Canals,[8] the latter four authors contributing but little to the procedure of Fresenius.

In view of the fact that no thoroughly reliable procedure has yet been described, it is not surprising to find in standard books on analysis such obviously incorrect statements as "At 500°, the oxalate begins to decompose, free carbon is liberated and calcium carbonate begins to form,"[9]

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[1] Winkler, *Z. angew. Chem.*, 31, [I], 187, 203 (1918).

[2] Szebelledy, *Z. anal. Chem.*, 70, 39 (1927).

[3] Ewe, *Chem. News*, 121, 53 (1920); *Am. J. Pharm.*, 92, 401 (1920).

[4] Fresenius, "A System of Instruction in Quantitative Chemical Analysis," 4th ed., John Churchill and Sons, London, 1865, p. 164.

[5] Irby, *Z. anal. Chem.*, 13, 56 (1874).

[6] Fram, *Chem.-Ztg.*, 21, 410 (1897).

[7] Brunck, *Z. anal. Chem.*, 45, 83 (1906).

[8] Canals, *Bull. soc. chim.*, [4] 23, 422 (1918).

[9] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 4th ed., 1925, p. 107.

while some authorities[10] are inclined to believe that while in careful hands the method will give accurate results, it requires much more careful attention than the oxide method, and hence will not commend itself widely.

Recent investigators, Foote and Bradley[11] and de Groot,[12] apparently believed that the only safe procedure was ignition in an atmosphere of carbon dioxide in a Rose crucible.

From Johnston's[13] measurements of equilibrium pressures of the thermal dissociation of calcium carbonate and from the partial pressure of carbon dioxide in air,[14] it can be shown that calcium carbonate is stable in air up to about 520". Likewise, the oxalate can be completely changed into carbonate by a prolonged ignition at a temperature as low as 430° as was shown by Irby.[5] It is to be expected, therefore, that conditions can be found under which ignition in air will result in complete and rapid conversion of calcium oxalate into carbonate, without any danger of decomposition of the latter into oxide. The purpose of this work was to investigate these conditions and the errors involved because, from the authors' experience, the precipitate is best weighed in this form.

Experimental

As a standard in this work, Kahlbaum's "Iceland Spar," consisting of **99.95%** calcium carbonate with magnesium and ferrous carbonate as main impurities, was used. The composition was checked by ignition of oxalate to oxide and by titration of oxalate with ceric sulfate.[15]

Samples ranging in weight from **0.2** to **0.9** g. were dissolved in **25** cc. of **1**:4 hydrochloric acid and the solution was diluted to **200** cc. Calcium oxalate was precipitated from the hot solution by adding to it slowly and with constant stirring twice the theoretical amount of pure ammonium oxalate, dissolved in **25** to **50** cc. of water, after which the solution was made just alkaline to methyl red by adding slowly with constant stirring a freshly filtered solution of **1:5** ammonium hydroxide. The solution was kept hot for two hours, filtered through **a** porcelaia filtering crucible (Type A2),[16] and the precipitate washed, either with hot 0.5% ammonium oxalate solution, or with cold water. The crucible containing the precipitate was dried at **110°**, and then ignited.

The ignitions were carried out in a Simon–Miiller crucible furnace[17] the temperature of which could be kept constant within less than 5° by maintaining a constant current through the heating coil with an accurate ammeter and a variable resistance in the circuit. This furnace was carefully calibrated in terms of current by means of a calibrated platinum–platinum-rhodium thermocouple, and the temperature–current calibra-

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[10] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, p. **502.**

[11] Foote and Bradley, THIS JOURNAL, 48, **676 (1926).**

[12] De Groot, **Chem.** *Weekblad,* 23, **456 (1926).**

[13] Johnston, THIS JOURNAL, 32, **938 (1910).**

[14] **Cf.** Clarke, "The Data of Geochemistry," U. S. Geological Survey **Bulletin. 695,** 1920, p. **47.**

[15] Willard and Young, THIS JOURNAL, 50,1333 **(1928).**

[16] Manufactured by the Staatliche Porzellanmanufaktur, Berlin.

[17] Simon and Müller, *Z. angew.* **Chem.,** 39, 1377 **(1926).**

tion curve was repeatedly rechecked during the process of this investigation. A number of ignitions were also carried out in a large electric muffle, calibrated in a similar way.

Ignitions were carried out at 350, 400, 450, 500, 550 and 600°, using two different samples at each temperature. In this series the crucible with the precipitate was ignited for one hour, cooled in a desiccator and weighed inside a closed weighing bottle, using a similar weighing bottle for counterpoise. It was then ignited for one hour longer, cooled, weighed and the process repeated once more. The results are given in Table I.

TABLE I

IGNITION OF CALCIUM OXALATE BETWEEN 350 AND 600°

No.	Iceland spar, g.	Temp. of ignition, °C.	Time of ignition, hours	Precipitate, g.	Wt. $CaCO_3$ (theory), g.	Error, mg.
1	0.6174	350	1	0.7594	0.6171	+142.3
			2	.7374		+120.3
			3	.7252		+108.1
2	.6511		1	.8158	.6508	+165.0
			2	.8059		+155.1
			3	.7940		+143.2
1	.8297	400	1	.8387	.8293	+ 9.4
			2	.8315		+ 2.2
			3	.8302		+ 0.9
2	.6454		1	.6524	.6451	+ 7.3
			2	.6454		+ 0.3
			3	.6452		+ .1
1	.5927	450	1	.5926	.5924	+ .2
			2	.5924		.0
			3	.5924		.0
2	.6382		1	.6382	.6379	+ .3
			2	.6381		+ .2
			3	.6379		.0
1	.9089	500	1	.9087	.9085	+ .2
			2	.9086		+ .1
			3	.9086		+ .1
2	.7721		1	.7716	.7717	− .1
			2	.7716		− .1
			3	.7715		− .2
1	.7561	550	1	.7540	.7557	− 1.7
			2	.7500		− 5.7
			3	.7465		− 9.2
2	.7967		1	.7955	.7963	− 0.8
			2	.7924		− 3.9
			3	.7887		− 7.6
1	.7820	600	1	.7556	.7816	− 26.0
			2	.7351		− 46.5
			3	.7160		− 65.6
2	.8432		1	.8153	.8428	− 27.5
			2	.7929		− 49.9
			3	.7783		− 64.5

Even at as low a temperature as 400°, a three-hour ignition gives practically quantitative results, if the sample is not too large. At 450 and 500°, respectively, one-hour ignition suffices for quantitative conversion into carbonate, but at 550° and above the results are low due to formation of oxide.

Calcium oxalate ignited in this way gives a product which is perfectly white in color. When, however, the precipitate is filtered through filter paper, which can be completely burned off in a muffle at 500° in thirty minutes, and then ignited for from one to twenty-four hours, the precipitate is gray, and the results are *2* to **3** mg. high, depending on the size of the sample. Ignition of C. P. calcium oxalate as purchased likewise results in the formation of a product which is gray in color.

The formation of this impurity has hitherto been explained on the assumption that the decomposition of oxalate results in the formation of a small amount of carbon.[9]

Since in our procedure no formation of this product took place, no attempt was made to determine its nature. It seems doubtful, however, that this product, so resistant to heating in air, is carbon, and it is suggested that it might be a stable polymer of carbon suboxide formed in decomposition of the oxalate.[18]

The influence of time of ignition at 500° is shown in Table II, which is self-explanatory.

TABLE II

IGNITION OF CALCIUM OXALATE AT 500°

No.	Iceland spar, g.	Time of ignition	Precipitate, g.	$CaCO_3$ (theory), g.	Error mg.
1	0.2194	30 min.	0.2192	0.2193	−0.1
2	.8812		.8821	.8808	+1.3
1	.5915	45 min.	.5913	.5912	+0.1
2	.8847		.8844	.8843	+ .1
3	.7040		.7038	.7037	+ .1
4	.4999		.4996	.4997	− .1
1	.3491	60 min.	.3487	.3489	− .2
2	.4913		.4913	.4911	+ .2
3	.5014		.5010	.5012	− .2
4	.7079		.7076	.7076	.0
1	.3863	18 hrs.	.3862	.3861	+ .1

The recommended procedure for the determination of calcium (in solutions of its pure salts) is as follows. Precipitate the oxalate by adding to the hot acid solution twice the theoretical amount of ammonium oxalate (or oxalic acid), and slowly neutralize with 1:5 ammonium hydroxide, using methyl red as indicator. Let the solution stand on the hot-plate

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[18] Cf. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1924, Vol. V, pp. 904–907.

for two hours, filter through a filtering crucible (or a Gooch), dry at 110° for thirty minutes and ignite in an electric muffle for one hour at a temperature between 475 and 500°. For the separation of calcium from other elements the usual methods are applicable, followed by ignition to carbonate as above.

This method has been used in this Laboratory for the last three years, both in research work and by the students in quantitative analysis, and has given very satisfactory results.

When an accurate thermocouple is not available, the furnace can be adjusted to the right temperature in the following simple way. Silver chloride melts at 455° and lead chloride at 501°; thus the correct temperature can be easily obtained by adjusting the oven to such a temperature that silver chloride will melt, but not lead chloride. The melting point can be detected with the following device. In a small pyrex tube sealed at one end place some anhydrous silver chloride powder (or lead chloride); insert into the tube two electrodes, made by sealing into pyrex tubes short pieces of platinum wire with copper wire leads, so that the ends of the electrodes reach the bottom of the tube containing the powder, but do not touch each other. The electrodes can be kept in place by putting between them and wrapping around them a piece of asbestos paper, so that the whole fits tightly into the glass tube. The "melting point detector" so prepared (see Fig. 1) is placed inside the oven, with the leads going outside and connected in series with two dry cells and a small flash-light bulb. At the melting point the molten mass establishes an electrical connection between the electrodes and the light glows. A fresh detector has to be used each time, since the anode is strongly attacked by chlorine.

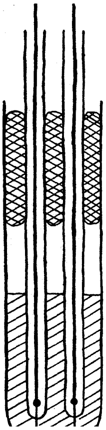

Fig. 1.—Melting point detector.

By the proper choice of material this simple method could be used to adjust the furnace to any desired temperature. It was tested in connection with this work and found to give very satisfactory results.

Summary

1. Ignition of calcium oxalate in air was studied at 350, 400, 450, 500, 550 and 600°.

2. Between 450 and 500° the oxalate is quantitatively converted into carbonate in one to two hours. This is made the basis of an accurate method for the gravimetric determination of calcium.

3. A simple method is described for adjusting a furnace to a desired temperature by utilizing the melting points of suitable salts.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE MICRO DETERMINATION OF HALOGENS AND METALS IN ORGANIC COMPOUNDS

BY H. H. WILLARD AND J. J. THOMPSON

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Hitherto, the Carius method has been the only accurate one available for the determination of halogens in all types of solid and liquid organic compounds. The method recently described by Thompson and Oakdale[1] has proved so accurate and satisfactory, even in the case of volatile liquids, that it seemed desirable to apply it to the micro determination of halogens. For the micro procedure we have devised a much more compact apparatus and as a result the method has become simpler and more rapid. A complete analysis, from the time of weighing the sample until the weight of silver halide is obtained, requires only forty-five to sixty minutes.

The principle involved is, as stated previously,[1] the use of fuming sulfuric acid as oxidizing agent, to which in certain instances persulfate is added. Any halide formed is then oxidized by permanganate or hydrogen peroxide to free halogen, which is absorbed in alkaline arsenite and subsequently precipitated as silver halide.

The micro determination is so simple, rapid and accurate that it seems likely to replace the classical Carius method.

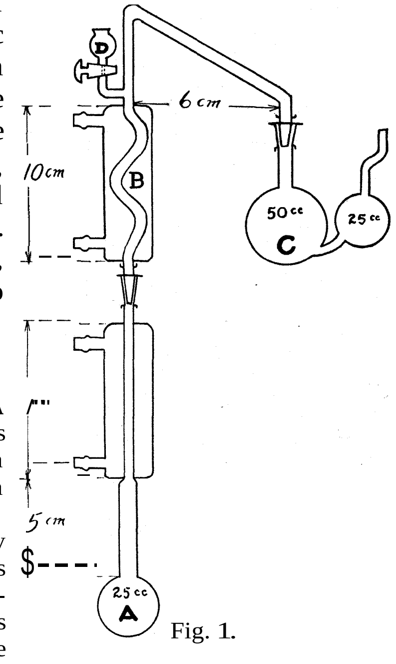

Fig. 1.

Experimental

The samples used weighed 15–25 mg. A micro balance was not required and weighings accurate to 0.01 mg. were quickly made on a Bunge air damped balance, type 4 DM, with a capacity of 200 g.

The apparatus used, which is made entirely of pyrex glass, is shown in Fig. 1. It consists of a 25-cc. flask provided with two small condensers and connected to two absorption bulbs by means of ground-glass joints, 7 mm. inside diameter. A small dropping funnel is fused to the top of the condenser.[1a] For much smaller samples the size of the apparatus can be reduced.

The Determining of Chlorine and Bromine.—If the compound is a solid, a sample of approximately 20 mg. or less is weighed into a micro beaker, about 6 X 7 mm., made from pyrex glass tubing. The sample and beaker are transferred to the decomposition flask

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[1] Thompson and Oakdale, THIS JOURNAL, 52, 1195 (1930).

[1a] This apparatus can be purchased from the Arthur H. Thomas Co., Philadelphia.

(A), Fig. 1. Five-tenths g. of potassium persulfate is then added[2] together with a few glass beads and a little copper sulfate. Section (B) is connected, and water passed through the condensers.[3] The absorption flask (C) contains 0.1 g. of arsenic trioxide to reduce halogen to halide,[4] 1 g. of chlorine-free sodium hydroxide and 15 cc. of water. Through the dropping funnel (D) 4 cc. of fuming sulfuric acid containing 20% SO_3 is added and the mixture is allowed to digest for fifteen minutes, keeping the sulfuric acid boiling gently. Then 5 cc. of concd. sulfuric acid (sp. gr. 1.84) is added. After the acid has become colorless and while it is boiling gently, an excess of a saturated solution of permanganate is added (2 cc. is usually sufficient), then 5 cc. of water. At this stage the condensers are emptied and the solution boiled until sulfur trioxide fumes appear. The apparatus is disconnected immediately, to prevent the joints from freezing, the contents of the absorption flask are transferred to a 100-cc. beaker and neutralized with dilute nitric acid (sp. gr. 1.10), using methyl orange as indicator. An excess of silver nitrate is added, then concd. nitric acid (sp. gr. 1.42) until there is an excess of 2 cc. The solution is boiled to coagulate the silver halide and filtered through a filtering crucible with a porous porcelain bottom,[5] washed with 1% nitric acid, then with acetone, dried at 135° and weighed.

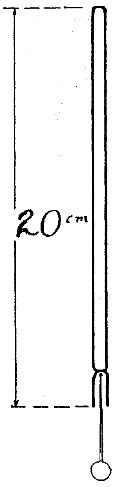

Fig. 2.

When liquid halogen compounds are to be analyzed, thin-walled bulbs are prepared. A bulb is filled by placing it and the liquid in a special apparatus.[1] The apparatus is evacuated through a side arm and then upon allowing the air to enter the apparatus the bulb is filled. Since the latter is too light to break by falling, it must be crushed somehow. A pyrex glass tube sealed off at both ends but having a pocket on one end to hold the stem of the bulb is used for this purpose (see Fig. 2). The bulb stem is placed in the pocket and then inserted into the flask which already contains the sulfuric acid, etc., and which is held horizontally. Care must be taken that the bulb does not fall out of the pocket. Both tube and crushed bulb are left in the apparatus until the determination is completed.

When chloroform or carbon tetrachloride is analyzed by this process, gaseous halogen compounds escape before complete reaction with sulfur trioxide occurs. This difficulty is surmounted by placing a narrow-bore quartz tube, about 20 cm. long, between the condenser and decomposition flask. Connection is made by heavy black rubber tubing. Heating the central portion of the tube to a red heat decomposes any organic halide gas and the halogen is completely absorbed.

The results of analyses of chlorine and bromine compounds are shown in Tables I and II. All the compounds used in this work were specially purified.

Determination of Iodine.—The procedure is identical with that for chlorine and bromine, except that no persulfate is added and an excess

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[2] Since the persulfate is usually contaminated with perchlorate, some of it being quite unfit for use, a blank determination is made, using a halogen-free organic compound, such as starch.

[3] All joints are well lubricated with a viscous paste, made by mixing phosphorus pentoxide with warm, sirupy phosphoric acid. See also Stephens, THIS JOURNAL, 52, 635 (1930). Rubber bands are used on the glass hooks.

[4] Honigschmid and Zintl, *Ann.*, 433, 201 (1923).

[5] These crucibles (type A1 is densest) are manufactured by the Staatliche Porzellan Manufaktur, Berlin. They were cut down to a height of approximately one centimeter and then weighed about 3 g.

TABLE I

RESULTS OF ANALYSES

Substance analyzed	Sample, mg.	AgCl, mg.	Chlorine, %	
			Calcd.	Found
$CHCl_3$	18.96	68.20	89.10	88.98
$CHCl_3$	28.71	103.27	89.10	88.98
CCl_4	14.64	54.57	92.20	92.20
CCl_4	12.96	48.28	92.20	92.15
$CH_3CONHCl$	18.16	27.76	37.92	37.81
$CH_3CONHCl$	19.21	29.41	37.92	37.87

TABLE II

RESULTS OF ANALYSES

Substance analyzed	Sample, mg.	AgBr, mg.	Bromine, %	
			Calcd.	Found
C_2H_5Br	35.66	61.41	73.34	73.29
C_2H_5Br	14.58	25.08	73.34	73.22
$C_2H_2Br_4$	25.06	54.42	92.47	92.41
$C_2H_2Br_4$	18.59	40.29	92.47	92.23
$CHBr_3$	21.02	46.86	94.85	94.87
$CHBr_3$	25.03	55.76	94.85	94.80

of halogen-free 10% hydrogen peroxide is used instead of permanganate. If persulfate is used, oxidation to non-volatile iodic acid occurs. The oxygen liberated from the peroxide expels the iodine from the apparatus and the hydriodic acid usually present is oxidized to free iodine. When a substance containing a very high percentage of iodine, such as iodoform, is analyzed in this way, some iodic acid is formed, due to insufficient organic reducing material. This may be remedied in either of two ways: first, by preventing the formation of iodic acid by adding 0.05 g. of starch to the iodine compound before decomposition begins; or, second, if iodic acid is formed, it is reduced, after all the iodine has been expelled from the apparatus, by adding a solution of hydrazine sulfate, followed by an excess of peroxide. For iodine determinations the dropping funnel (D) is conveniently sealed at the top of condenser (A) instead of (B).

TABLE III

RESULTS OF ANALYSES

Substance analyzed	Sample, mg	AgI, mg.	Iodine, %	
			Calcd.	Found
CHI_3	22.52	40.24	96.70	96.60
CHI_3	26.06	46.59	96.70	96.64
$C_{12}H_{10}SbI$	19.31	11.24	31.51	31.51
$C_{12}H_{10}SbI$	17.98	10.47	31.51	31.48
$C_{12}H_{10}AsI$	22.24	14.66	35.66	35.63
$C_{12}H_{10}AsI$	19.59	12.92	35.66	35.65

Micro Determination of Metals in Metallic Organic Halides.—If metals are to be determined the procedure is the same except that copper sulfate need not be added. Arsenic was determined in diphenylarsyl iodide in the following manner. The residual liquid in flask (A) after removal of halogen was transferred to a 150-cc. conical flask, the arsenic pentoxide was reduced to the trivalent state with sulfur dioxide, the solution diluted to 75 cc., boiled to remove the excess, 10 cc. of concd. hydrochloric acid was added and the arsenic trioxide titrated at 80° with $N/100$ potassium bromate, using methyl orange as indicator.[6]

If only arsenic is to be determined it is best to decompose the compound and reduce the arsenic entirely in the original flask (A). The iodine is expelled with 30% hydrogen peroxide and the arsenic pentoxide is reduced by adding an excess of solid hydrazine sulfate,[7] which in turn is destroyed by heating the solution to 250° for ten minutes. Antimony in diphenylstibyl iodide is determined in the same manner as the arsenic. The results are shown in Table IV.

TABLE IV

RESULTS OF ANALYSES

Substance	Sample, mg.	Metal present, %	Found, %
$C_{12}H_{10}SbI$	22.18	30.23 Sb	30.05
$C_{12}H_{10}SbI$	20.32	30.23 Sb	29.98
$C_{12}H_{10}AsI$	19.59	21.05 As	21.25
$C_{12}H_{10}AsI$	34.03	21.05 As	20.96
Selenium and $CHBr_3$	26.42	97.87 Se	97.72

It seemed desirable to apply this method to the determination of selenium in organic compounds containing halogens. Because no organic compound containing selenium was available, pure selenium powder was mixed with bromoform and the mixture decomposed by heating with 2 cc. of fuming and 3 cc. of concd. sulfuric acid. The bromine was liberated by permanganate and absorbed as usual. The selenic acid remaining in the flask was determined by reduction to metallic selenium[8] with an excess of hydroxylamine hydrochloride and determined gravimetrically. No volatilization of selenium occurred in the presence of bromine. Results are shown in Table IV.

Summary

1. A micro method has been described for the determination of halogens in solid or liquid organic compounds, based upon oxidation of the sample with fuming sulfuric acid. The halogen is distilled into alkaline arsenite and then precipitated as silver halide.

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[6] Gyory, *Z.* anal. Chem., 32, 415 (1893). Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., N. Y., 1929, Vol. II, p. 580. This is simpler and more rapid than the method suggested by Cislak and Hamilton [THIS JOURNAL, 52, 637 (1930)] and equally accurate.

[7] Schulek and Villecz, *Z.* anal. Chem., 76, 81 (1929).

[8] Lenher and Kao, THIS JOURNAL, 47, 2454 (1925); Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 265.

2. Metals may be determined in the same solution from which the halogen has been removed.

3. A more compact apparatus can be used and the whole process is simpler and more rapid than in the macro method previously described.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

AN APPLICATION OF MOVING BOUNDARIES TO A STUDY OF AQUEOUS MIXTURES OF HYDROGEN CHLORIDE AND POTASSIUM CHLORIDE

BY L. G. LONGSWORTH[1]

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Introduction

The purpose of this research was the measurement of the mobilities of the various ion constituents in aqueous mixtures of hydrogen and potassium chlorides. Since the conductances of such solutions do not follow the law of mixtures, it appeared of interest to determine which ion constituents were responsible for these deviations. The moving boundary method was employed in these determinations, boundaries of the rising type being used exclusively. The results, as will be shown below, are also of interest in connection with the recent work on the separation of the rare earth elements by the ionic migration method.[2]

Theoretical

The electrolysis of a mixture of hydrogen and potassium chlorides, using, for instance, a cadmium anode as the source of indicating cations, may be represented diagrammatically as follows. The use of the metallic anode in this manner is the method of Cady and Longsworth,[3] though the source of indicating ions may also be a solution of an appropriate electrolyte. Both methods were employed in these experiments. The tube is initially filled throughout with the mixture of uniform composition as shown in Fig. 1. After current has passed for a time, the hydrogen-ion constituent originally in the lower part of the tube will, due to its high mobility, have forged ahead of a portion of the potassium-ion constituent, and there should be the two boundaries, A and B, as shown in Pig. 2. These two boundaries have been observed and their separate progress has been followed quantitatively.

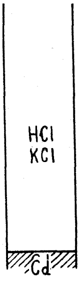

Fig. 1.

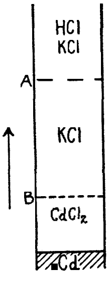

Fig. 2.

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[1] National Research Council Fellow.

[2] Kendall and Clarke, *Proc. Nat. Acad. Sci.*, 11, 393 (1925); Kendall and Crittenden, *ibid.*, 9, 75 (1923); Kendall and White, *ibid.*, 10, 458 (1924).

[3] Cady and Longsworth, THIS JOURNAL, 51, 1656 (1929).

The boundary A divides the mixture originally placed in the tube from a region of pure potassium chloride. This boundary travels with a velocity determined by the mobility of the hydrogen-ion constituent and the potential gradient in the mixture.

The slower boundary B is the usual boundary between the indicating electrolyte formed by the electrochemical oxidation of the cadmium anode and a pure potassium chloride solution. The boundary B travels with a velocity determined by the mobility of the potassium-ion constituent and the potential gradient prevailing at the "adjusted" concentration C'_{K} of the region between the two boundaries. This adjusted concentration can be computed from the expression

$$\frac{C'_{\mathrm{K}}}{T'_{\mathrm{K}}} = \frac{C_{\mathrm{H}}}{R_{\mathrm{H}}} + \frac{C_{\mathrm{K}}}{R_{\mathrm{K}}}$$

in which C denotes concentration, T the transference number and R is a function of the ion mobilities. A derivation of this expression follows.

Throughout this treatment the velocity of an ion constituent will be used. This velocity is a measurable quantity. The velocity of an individual ion cannot, at present, be determined experimentally. If the electrolyte is completely dissociated, the velocity of an ion constituent is identical with the individual ion velocity. If incompletely dissociated, the two velocities differ by a factor equal to the degree of dissociation

Let V_{H} represent the observed velocity of the hydrogen-ion constituent and U_{H} the mobility of this ion constituent, then

$$V_{\mathrm{H}} = U_{\mathrm{H}}\frac{\mathrm{d}E}{\mathrm{d}x}, \textit{ and } A_H = FU_{\mathrm{H}}$$

where Λ_{H} is the conductance of 1 g. equivalent of hydrogen ion. F is the faraday in coulombs if U_{H} is expressed in practical units. The total hydrogen-ion concentration in gram equivalents per milliliter of solution is denoted by C_{H} and the same symbols with appropriate subscripts refer to corresponding quantities for the potassium- and chloride-ion constituents. If A is the (uniform) cross-sectional area in square centimeters of the tube in which electrolysis is taking place, the current flowing in the tube is

$$I = FA(C_{\mathrm{H}}V_{\mathrm{H}} + C_{\mathrm{K}}V_{\mathrm{K}} + C_{\mathrm{Cl}}V_{\mathrm{Cl}}) \tag{1}$$

The electro-neutrality of the solution is expressed by

$$C_{\mathrm{H}} + C_{\mathrm{K}} = C_{\mathrm{Cl}} \tag{2}$$

If x denotes distance along the tube, the quantity of hydrogen ion, Q_{H}, passing through a given cross section at x in At seconds is

$$Q_H = (AC_{\mathrm{H}}V_{\mathrm{H}})\Delta t \tag{3}$$

and at x + Ax

$$Q_{\mathrm{H}} + \Delta Q_{\mathrm{H}} = \left[(AC_{\mathrm{H}}V_{\mathrm{H}}) + \frac{\partial}{\partial x}(AC_{\mathrm{H}}V_{\mathrm{H}})\,Ax\right]\Delta t \tag{4}$$

The change in hydrogen-ion content within the region between x and x + Ax is given by the difference between (3) and (4)

$$\Delta Q_{\mathrm{H}} = -\frac{\partial}{\partial x}(AC_{\mathrm{H}}V_{\mathrm{H}})\Delta x\Delta t$$

Since the corresponding concentration change, ΔC_{H}, is equal to ΔQ_{H} divided by the volume, $A\Delta x$, in which the change occurs

$$\Delta Q_{\mathrm{H}} = A\Delta x\Delta C_{\mathrm{H}} = -\frac{\partial}{\partial x}(AC_{\mathrm{H}}V_{\mathrm{H}})\Delta x\Delta t \tag{5}$$

In the limit, Equation 5 becomes

$$A\frac{\partial C_{\mathrm{H}}}{\partial t} + \frac{\partial}{\partial x}(AC_{\mathrm{H}}V_{\mathrm{H}}) = 0 \tag{6}$$

and similarly for the potassium-ion constituent

$$A\frac{\partial C_{\mathrm{K}}}{at} + \frac{a}{at}(AC_{\mathrm{K}}V_{\mathrm{K}}) = 0 \tag{7}$$

Multiply (6) by $F(V_{\mathrm{H}} + V_{\mathrm{Cl}})/V_{\mathrm{H}}$ and (7) by $F(V_{\mathrm{K}} + V_{\mathrm{Cl}})/V_{\mathrm{K}}$, assuming the ratios $(V_{\mathrm{H}} + V_{\mathrm{Cl}})/V_{\mathrm{H}}$ and $(V_{\mathrm{K}} + V_{\mathrm{Cl}})/V_{\mathrm{K}}$ to be independent of the concentration, and add the resulting equations

$$AF\frac{V_{\mathrm{H}} + V_{\mathrm{Cl}}}{V_{\mathrm{H}}}\frac{\partial C_{\mathrm{H}}}{\partial t} + AF\frac{V_{\mathrm{K}} + V_{\mathrm{Cl}}}{V_{\mathrm{K}}}\frac{\partial C_{\mathrm{K}}}{\partial t} + \frac{\partial}{\partial x}[FAC_{\mathrm{H}}(V_{\mathrm{H}} + V_{\mathrm{Cl}})] + \frac{\partial}{\partial x}[FAC_{\mathrm{K}}(V_{\mathrm{K}} + V_{\mathrm{Cl}})] = 0$$

Collecting terms and setting $1/R_{\mathrm{H}} = (V_{\mathrm{H}} + V_{\mathrm{Cl}})/V_{\mathrm{H}}$ and $1/R_{\mathrm{K}} = (V_{\mathrm{K}} + V_{\mathrm{Cl}})/V_{\mathrm{K}}$,[4]

$$\frac{AF}{R_{\mathrm{H}}}\frac{\partial C_{\mathrm{H}}}{\partial t} + \frac{AF}{R_{\mathrm{K}}}\frac{\partial C_{\mathrm{K}}}{\partial t} + \frac{\partial}{\partial x}[FA(C_{\mathrm{H}}V_{\mathrm{H}} + C_{\mathrm{K}}V_{\mathrm{K}} + C_{\mathrm{H}}V_{\mathrm{Cl}} + C_{\mathrm{K}}V_{\mathrm{Cl}})] = 0 \tag{8}$$

From *(1)* and (2) it is seen that the bracketed expression in (8) is the current **I**, and since this is uniform throughout the tube

$$\frac{\partial I}{\partial x} = 0$$

The resulting differential equation can then be integrated to give

$$\frac{C_{\mathrm{H}}}{R_{\mathrm{H}}} + \frac{C_{\mathrm{K}}}{R_{\mathrm{K}}} = \text{constant} + f(x) \tag{9}$$

This corresponds to, but is not identical with, the "beharrlichen" function of Kohlrausch.[5] For any given value of x it retains its initial value (neglecting diffusion and convection) throughout electrolysis. If the composition of the solution originally present in the tube is uniform, $f(x)$ also becomes constant. Application of this function, which will henceforth be termed the "regulating" function, to the experiments described here yields the relation

$$\frac{C_{\mathrm{H}}}{R_{\mathrm{H}}} + \frac{C_{\mathrm{K}}}{R_{\mathrm{K}}} = \frac{C'_{\mathrm{K}}}{T'_{\mathrm{K}}} = \text{constant} \tag{10}$$

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[4] The symbol R is identical with the transference number for a simple binary electrolyte but is not the transference number of an ion constituent in a mixture. In the latter case the transference number is given by a more complicated expression; see D. A. MacInnes, THIS JOURNAL, 47, 1922 (1925).

[5] Kohlrausch, Ann. *Physik,* 62, 209 (1897).

The primed quantities in (10) refer to the region of pure potassium chloride solution between the two boundaries, A and B, Fig. 2.

In connection with this regulating function it should be pointed out that the derivations given by Kohlrausch[5] and von Laue[6] are based on the Arrhenius theory of solutions of electrolytes with the attendant assumption of constant ion mobility. Experimentally, the mobility of an ion constituent varies more rapidly with the concentration than does a ratio of these mobilities. Consequently the assumption of R independent of concentration is a more limited assumption than the constancy of the individual mobilities. Otherwise the treatment given here is similar to that of von Laue and the generalized Equation 5, page **332,** in his development is identical in form with Equation 9.

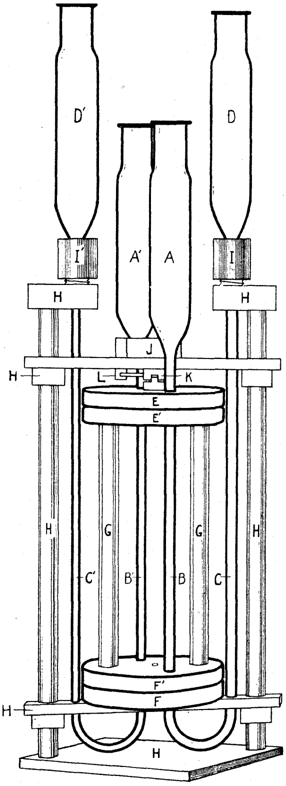

Fig. 3.

The Moving Boundary Apparatus

The cell used for these measurements in which the source of indicator ion is a solution is shown in Fig. **3.** The shearing mechanism of MacInnes and Brighton[7] was utilized for forming the boundary. The plate glass disks EE' and FF' are etched in the manner described by these authors and the electrode chambers AA'D and D' are designed according to their recommendations. Tubes B and B' are graduated[8] and calibrated tubes in which the motion of the boundary is observed. The system ABCD is quite independent of the system A'B'C'D', the tube B having an average cross-sectional area about twice that of B'. Only one of these tube systems is used in a determination. The glass disks E' and F', together with the brass supporting rods GG and the tubes BB', constitute an independent unit of the cell and may be removed for cleaning. By clamping this central unit to the lower disk F and turning E over E', boundaries may be formed which can reach the graduations by descending. On the other hand, clamping the central unit to the upper disk E and turning F' over F gives rise to boundaries that can be observed if they ascend the tube. The cell may thus be adapted for the study of either rising or falling boundaries, though all observations made in this paper were on the first mentioned type.

The parts H are of brass and constitute the supporting framework for the glass parts of the cell which are traced in heavier lines. I and I' are threaded bakelite couplings to permit removal of the electrode chambers D and D' for cleaning.

The manipulation using the tube system ABCD and observing a rising boundary is as follows. The plates E and E' are lubricated and clamped together with the tube B

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[6] M. von Laue, Z. *anorg. Chem.*, **93,** 329 (1915).

[7] MacInnes and Brighton, THIS JOURNAL, 47, 994 (1925).

[8] MacInnes, Cowperthwaite and Huang, *ibid.*, 49, 1710 (1927).

and chamber **A** in alignment. This unit is then filled with the solution whose transference number is to be determined. The tube C and chamber D are filled with solution of indicator electrolyte. Silver-silver chloride electrodes are introduced into the electrode chambers and, if necessary, a few milliliters of a more concentrated solution introduced around these electrodes. The disks F and F′ are then lubricated and pressed together with the protruding drops of solution from B and C in their respective recesses in the opposite disk, as described by MacInnes and Brighton.[7] The cell is then placed in a vibration-free thermostat and allowed to come to thermal equilibrium. Potential is then applied and the circuit tested to see that no current is flowing. The boundary is next formed in the following manner.

A coil spring **J** of phosphor bronze furnishes power for shearing the plate glass disks in initially forming the boundary. The brass coupling K transmits this power to the disk, also permitting the removal of the disk, E, together with the electrode chambers **AA'** which are sealed into it, for cleaning. **A** release mechanism L is operated by a flexible camera shutter cable (not shown in the diagram). This arrangement permits the turning of the plates and the formation of the boundary without starting vibration. The desirability of such an arrangement has been discussed by MacInnes, Cowperthwaite and Shedlovsky.[9] Upon the release of the spring tension, due to the viscosity of the lubricant between the plates, the plate F′, together with the cell units rigidly connected to it, smoothly turns about its center until tube B is exactly over tube C. The boundary is thus formed and starts to rise immediately, since the electrical circuit is now complete.

For rising boundaries where, according to the method described by Cady and Longsworth,[3] a metallic anode is used as the source of indicator ions, a similar cell was employed. It differs from the one just described in that a cylindrical recess was ground in the lower plate glass disk in which a small disk of anode metal was placed, and also in that no shearing mechanism is necessary.

The current through the cell was maintained constant throughout a determination by means of an improved constant current regulator.[10] This regulator is a modification of the apparatus used by MacInnes, Cowperthwaite and Blanchard,[11] modified so as to give a constant current in a circuit in which both increases and decreases of resistance may occur.

Materials and Purification.—The potassium chloride was recrystallized twice from conductivity water and fused in a platinum crucible. The hydrochloric acid was a pure product, diluted to constant boiling strength and distilled, the end fractions being rejected as recommended by Foulk and Hollingsworth.[12] The concentration of this constant boiling acid was interpolated from the data of these authors.

The materials used as indicators were treated as follows. The potassium iodate was recrystallized from water and dried over phosphorus pentoxide in *vacuo.* The sodium salt of iodeosin (tetra-iodofluorescein) was especially prepared by the makers and was further purified by four recrystallizations from water in this Laboratory. The cadmium metal and iodic acid were of a good grade and were not further purified.

Conductivity Measurements.—The conductances of the solutions were measured on the shielded bridge developed by Dr. Theodore Shedlovsky of these Laboratories Since this bridge has been described in a separate communication,[13] the following brief notes will suffice here. Pipet cells of the Washburn type were calibrated with 0.1 demal potassium chloride solution according to the recommendations of Parker and

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[9] MacInnes, Cowperthwaite and Shedlovsky, THIS JOURNAL, **51,** 2671 (1929).

[10] Longsworth and MacInnes, J. Opt. *Soc. Am.,* 19, 50 (1929).

[11] MacInnes, Cowperthwaite and Blanchard, THIS JOURNAL, 48, 1909 (1926).

[12] Foulk and Hollingsworth, ibid., **45,** 1220 (1923).

[13] Shedlovsky, ibid., 52, 1793 (1930).

Parker.[14] An audion oscillator operating at a frequency of 2000 cycles supplied the bridge current, which was amplified by two stages of audio frequency amplification before passing to the telephones. The bridge was of the direct reading type with equal ratio arms. The thermostat in which the conductivity cells were immersed was filled with oil. The temperature was maintained constant at 25 ± 0.002°. The temperature was determined by means of a carefully calibrated platinum resistance thermometer.

Rising Boundaries.—Since MacInnes, Cowperthwaite and Huang,[8] working with rising boundaries, observed convection currents due to heating, it seemed necessary to investigate this effect in detail. Their experiment with a rising boundary between potassium chloride and potassium permanganate, used as indicator electrolyte, was repeated and the same phenomena were observed. These were a diffuse color margin, and a "chimney" tinged with the purple color of the permanganate ion in the potassium chloride solution above the boundary. However, I have found that when the much heavier and less mobile iodeosin ion is substituted for the permanganate ion, an extremely sharp margin results with no trace of the intense red color of this ion in the colorless solution in advance of the boundary. The iodeosin ion has been used as an indicator by Franklin and Cady.[15]

If the mobilities of the chloride- and permanganate-ion constituents, and also the densities of the two solutions under the conditions of the experiment, are compared, it appears quite likely that the differences in these properties are not great enough to permit the development of an effective margin. An effective moving boundary results when the restoring effect due to the potential gradient change at the boundary is strong enough to overcome the disturbing effects of convection, diffusion and, possibly, electro-osmosis. The restoring effect has been described in a paper by MacInnes and Cowperthwaite.[16]

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[14] Parker and Parker, THIS JOURNAL, 46, 312 (1924).

[15] Franklin and Cady, *ibid.*, 26, 499 (1904).

[16] MacInnes and Cowperthwaite, *Proc. Nat. Acad. Sci.*, 15, 18 (1929). These authors find experimentally that upon interruption of the current the two solutions forming the boundary begin to diffuse into each other. However, though the current may be interrupted for as much as thirty minutes, upon closing the circuit again the boundary reforms and soon recovers its original sharpness. After reformation and during the period between the reclosing of the circuit and the return to its original sharpness, the boundary moves at the correct velocity. The authors explain this restoring effect of the current as due to the change of potential gradient occurring at the boundary. The lower specific conductance of the indicator solution means a steeper potential gradient in this region. If a more mobile ion in front of the boundary diffuses into the indicator region, it will be subject to a steeper potential slope and will forge ahead of the surrounding less mobile indicator ions until it has regained the boundary. Conversely, if an indicator ion diffuses across the boundary into the region of lower potential slope prevailing in the solution under observation, it will, of necessity, lag behind until it has fallen back into the indicator region. This restoring mechanism of the potential gradient change at the boundary tends to keep the two ion constituents separated and the boundary sharp.

With rising boundaries mixing due to convection will be greater than with falling boundaries because with the former the hotter solution is underneath, an arrangement which tends to produce circulation in the cooler solution. Due to this greater tendency to mix, the restoring effect must, therefore, be greater in rising boundaries. However, mixing of the two solutions at the boundary will be decreased if there is a large difference in the density of those solutions. The choice of the proper indicator will, therefore, be a matter of experiment. For the determination of the anion mobilities in the solutions studied in this investigation, iodic acid and potassium iodate were used as the indicating electrolytes. The low mobility of the iodate-ion constituent and the high density of the solutions of its salts apparently eliminated the troubles, mentioned above, due to heating and convection.

One important advantage of rising boundaries over the descending type is the wider concentration range throughout which there is automatic concentration adjustment of the indicator solution. It is, therefore, not so necessary to make determinations at a series of indicator electrolyte concentrations as when working with falling boundaries. The data of Table I show the effect of indicator-ion concentration upon the observed anion transference number of potassium chloride at 0.1 normal or 0.1 g. equivalent per liter of solution. This unit of concentration differs from the one defined in the theoretical part by a constant factor of 10^{-3}, that is, for 0.1 normal potassium chloride, $C_{KCl} = 10^{-4}$. From Table I the transference number is seen to be independent of the concentration of the indicator solution of potassium iodate if the latter is between about 0.06 and 0.15 normal. A normality of about 0.06 is the value required by the "regulating" function applied to this simple boundary. To understand why concentration adjustment over such a wide range is not attained in the case of falling boundaries, let us consider the following comparison of the two methods.

TABLE I

THE EFFECT OF THE INDICATOR CONCENTRATION ON THE OBSERVED TRANSFERENCE NUMBER OF POTASSIUM CHLORIDE

Normality		dE/dx	
KCl	KIO_3	volts/cm.	T_a
0.1	0.05	3.086	[a]
.1	.066	3.692	0.5100
.1	.075	3.995	.5103
.1	.1	3.086	.5100
.1	.1	4.298	.5101
.1	.15	4.298	.5106
.1	.2	4.298	.5120

[a] Margin quite distorted and computed value of T_a changed from 0.532 at beginning of run to 0.513 at the close.

If a margin is formed between 0.1 normal potassium iodate and 0.1 normal potassium chloride, Fig. 4 represents the initial condition. On passage of a current the boundary will rise and after some time Fig. 5 will represent the new conditions in the tube. That is, a concentration gradient between 0.1 normal and 0.06 normal potassium iodate will remain at C. Since the relation of the densities d are $d_{0.1\,N\,\mathrm{KCl}} < d_{0.06\,N\,\mathrm{KIO_3}} < d_{0.1\,N\,\mathrm{KIO_3}}$, the lighter solution is on top and this distribution will not be disturbed by gravity. On the other hand, consider an analogous case for falling boundaries where the boundary is initially formed between 0.1 normal potassium chloride and 0.1 normal lithium chloride, Fig. 6. After the boundary has fallen some distance, Fig. 7 would represent conditions were it not for the fact that a denser solution of lithium chloride would' thus be left on top. These two solutions of lithium chloride would consequently tend to mix and destroy the concentration adjustment as fast as it was made. Both rising and falling boundaries are found, however, to give erroneous results when the indicator-ion concentration is initially too low.

Fig. 4.

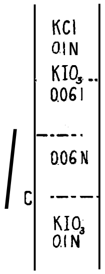

Fig. 5.

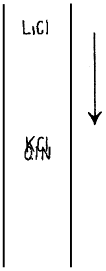

Fig. 6.

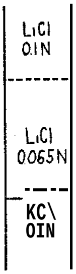

Fig. 7.

Experimental Results

Table II contains the results of transference measurements on the anion constituents. The chloride-ion concentration in all mixtures was maintained at 0.1 normal. The composition of the mixtures will be indicated by the ratio y of hydrogen-ion content to the chloride-ion content, that is, $y = C_{\mathrm{H}}/C_{\mathrm{Cl}}$ and $(1 - y) = C_{\mathrm{K}}/C_{\mathrm{Cl}}$. The indicator solutions for the anion constituents of the mixtures were made up to a total iodate-ion concentration of 0.1 normal, the ratio of hydrogen to potassium-ion content in these solutions being the same as that of the solution for which they were to serve as indicators.

TABLE II

CHLORIDE-ION CONDUCTANCE IN MIXTURES OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE AT A TOTAL CONCENTRATION OF 0.1 N AND 25°

Solution $C_{\mathrm{H}}/C_{\mathrm{Cl}}$	T_{Cl}	Λ	Λ_{Cl}	Λ_{Cl} (calcd.)
1.00	0.1693	391.28	66.32*	...
0.75	.2041	324.31	66.19	66.18
.50	.2560	258.07	66.07	66.03
.25	.3414	192.83	65.83	65.89
.00	.5101	128.89	65.75	...

The value of Λ_{Cl} marked with an asterisk is computed from the value of $T_{\mathrm{H}} = 0.8305$ recorded in Table III. This value is given preference since it is the mean of a larger number of determinations. Comparison of the results for the solutions of pure hydrogen chloride and pure potassium chloride as given in Tables 11, III and V shows that $T_c + T_a = 0.9998$ for the former and 0.9999 for the latter. The deviation from the theoretical value of unity is within the experimental error.

From Table II it is seen that Λ_{Cl} from 0.1 normal hydrogen chloride is slightly higher than from 0.1 normal potassium chloride. This is at variance with the constant value of Λ_{Cl} from these two salts found by MacInnes and Smith.[17] The author, however, has determined the chloride-ion conductance from a series of uni-univalent chlorides over the concentration range from 0.1 to 0.02 normal. The results deviate by a few tenths of one per cent. from the constancy found by MacInnes and coworkers at the higher concentration. These deviations from constancy tend to disappear, however, as the concentration is reduced. The chloride-ion conductance from these uni-univalent chlorides seems to be a function of the conductance of the co-ion.

The values of Λ_{Cl} quoted in the last column of Table II were computed on the basis of linear variation between the chloride-ion conductances in pure hydrogen chloride and pure potassium chloride solutions. The conductance of the chloride-ion constituent in the mixtures is thus seen to vary linearly between its values in the pure solutions. This is in complete agreement with the findings of MacInnes, Cowperthwaite and Shedlovsky[S] on mixtures of sodium chloride and potassium chloride. These authors find that though the conductances of the mixtures deviate from additivity, the conductance of the chloride ion remains constant. In other words, the mobility of the common ion constituent is not the cause for the deviation from additivity of the conductances of mixtures of this valence type.

Table III contains the results of observations on the leading boundary A of Fig. 2. As explained in a preceding section, this boundary is that which arises between the mixture of acid and salt and the region of pure potassium chloride. This boundary was visible as a refraction margin in only one of the mixtures (y = 0.75), where it was faint but sharp. In the other two mixtures the progress of this boundary was ascertained by

TABLE III

HYDROGEN-ION CONDUCTANCE IN MIXTURES OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE AT A TOTAL CONCENTRATION OF 0.1 N AND 25°

Solution C_H/C_{Cl}	AH	$y\Lambda_H$	$T_H = y\,\Lambda_H/\Lambda$
1.00	324.96	324 96	0.8305
0.75	322.4	241.8	,7456
.50	319.9	159.9_5	.6198
.25	316.9	79.2_3	.4109
.00	...	0.00	.0000

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[17] MacInnes and Smith, THIS JOURNAL, 47, 1009 (1925).

the color change induced in a trace of methyl violet introduced into the solution. In Table IV are given data showing that the presence of the trace of dye did not materially affect the progress of the boundary in the one mixture where direct comparison could be made. V'_A and V'_B of Table IV are quantities proportional to the velocities of the boundaries **A** and B, respectively, Fig. 2.

TABLE IV

EFFECT OF PRESENCE OF METHYL VIOLET ON THE BOUNDARY VELOCITIES IN THE MIXTURE 0.075 N HCl–0.025 N KCl

Experiment No.	Dye present 1	2	← Dye absent → 3	4	5
V'_A	9954	9952	9952	..	..
V'_B	7055	7055	7063	7058	7057

The equivalent conductance Λ_K of the potassium-ion constituent in the mixtures may be computed by the relation

$$(1 - y)\,\Lambda_K = \Lambda - \Lambda_{Cl} - y\Lambda_H$$

These values, together with those of the other ion constituents, are collected in Table V.

TABLE V

CONDUCTANCE OF THE ION CONSTITUENTS OF MIXTURES OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE AT A TOTAL CONCENTRATION OF 0.1 N AND 25°

Solution C_H/C_{Cl}	$(1 - y)\,\Lambda_K$	T_K	Λ_H	Λ_K	Λ_{Cl}
1.00	0.00	0.0000	324.96	65.5*	66.32
0.75	16.3	.0503	322.4	65.2	66.19
.50	32.0_5	.1242	319.9	64.1	66.07
.25	47.8	.2477	316.9	63.7	65.83
.00	63.14	.4898	314.0*	63.14	65.75

The values marked with an asterisk are extrapolated, assuming linear variation with the concentration of that constituent. They represent, respectively, the equivalent conductance of vanishingly small quantities of hydrogen ion in 0.1 normal potassium chloride and of potassium ion in 0.1 normal hydrochloric acid.

As the experimental work here presented was being completed, Bennewitz, Wagner and Kuchler[18] reported an extension of the Onsager[19] equations for the conductance of strong binary electrolytes to the case of a ternary ion mixture in which one ion constituent is present in very small quantities. The theory, as developed, is valid only at high dilutions where the equivalent conductance varies as the square root of the concentration. To extrapolate from this region of validity to 0.1 normal solutions can yield predictions of only a qualitative nature. In any event, their theory predicts that the equivalent conductance of vanishingly small quantities of hydrogen ion in 0.1 normal potassium chloride will be

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[18] Bennewitz, Wagner and Kuchler, *Physik. Z.*, 30, **623 (1929).**

[19] Onsager, *ibid.*, **27,** 388 **(1926); 28, 277 (1927).**

less than in 0.1 normal hydrogen chloride, while the conductance of the potassium ion will be slightly increased in going from 0.1 normal potassium chloride to 0.1 normal hydrogen chloride. Reference to Table V shows that the extrapolated ion conductances are in qualitative agreement with their theory.

Concentration Changes and Test of the Regulating Function

Referring once more to Fig. 2, if the theoretical treatment leading to Equation 10

$$\frac{C_H}{R_H} + \frac{C_K}{R_K} = \frac{C'_K}{T'_K}$$

is valid, this equation provides a means for computing the "adjusted" concentration C'_K from the ionic mobility relationships across the boundary A and the known concentrations above this leading boundary. Since the leading solution of boundary B is the indicator solution of boundary A, this adjusted concentration C'_K can also be computed independently from observations on the motion of boundary B. If the results of the two methods agree, this is evidence for the correctness of Equation 10, which is an expression of the "regulating" function.

For a boundary between two simple solutions such as those meeting at the boundary B, there is the relation

$$T = \frac{VCF}{It} \tag{11}$$

In this equation, T is the transference number, V the volume swept through by the boundary in t seconds and the other terms represent, as before, the concentration, the faraday and the current. It is evident, therefore, that if T is known, the concentration C may be found. From the observed velocity of the boundary B and the independently determined transference number of potassium chloride over the range of concentrations involved, C'_K has been computed by means of Equation **11.** If the transference number changed very rapidly with the concentration, such a computation would require a series of approximations. For potassium chloride solutions, however, the transference number varies so slightly with concentration that one approximation is sufficient. The concentrations thus obtained are given in Col. 4 of Table VI, which also includes the data necessary for these computations. These data are the

TABLE VI

DETERMINATION OF THE "ADJUSTED" CONCENTRATION OF THE REGION OF PURE POTASSIUM CHLORIDE SOLUTION FORMED ON ELECTROLYSIS OF MIXTURES OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE

Solution C_H/C_{Cl}	VF/It	T'_K	$C'_K \times 10^6$
0.75	7065	0.4897	69.31
.50	6154	.4898	79.59
.25	5452	.4899	89.86

values of VF/It determined experimentally from the velocity of B, and the independently determined values of T'_K for pure potassium chloride solutions.

For comparison the values of C'_K (2) calculated by means of Equation 10 are recorded in Col. 7 of Table VII. The values of R_H and R_K used in this calculation and recorded in Cols. 2 and 4 are computed from the data of Table V. Reference to the values of the ion conductances given in Table V indicates, however, that the velocity ratio, $V_K(V_K + V_{Cl}) = \Lambda_K/(\Lambda_K + \Lambda_{Cl})$, is slightly different on the two sides of the boundary A. Thus the assumption as to the constancy of this ratio is only an approximation, but a rather close one in this case. The values of C'_K **(3)** recorded in the last column of Table VII are computed assuming the ratio R_K to remain constant on the two sides of the boundary A and equal to T'_K, the ratio or cation transference number in pure potassium chloride at the "adjusted" concentration C'_K. The independently computed values *(1)* are copied from Table VI to facilitate comparison.

TABLE VII

TEST OF THE REGULATING FUNCTION FOR MIXTURES OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE

$C_H \times 10^6$	R_H	$C_K \times 10^6$	R_K	T_K'	$C'_K \times 10^6$ (1)	$C'_K \times 10^6$ (2)	$C'_K \times 10^6$ (3)
75	0.8296	25	0.4962	0.4897	69.31	68.93	69.27
50	.8288	50	.4923	.4898	79.59	79.29	79.55
25	.8281	75	.4919	.4899	89.86	89.49	89.79

In Table VII the agreement between the independently computed values for the adjusted concentration of the region of pure potassium chloride solution between the two boundaries is quantitative evidence for the validity of the regulating function (Equation *10)* under the conditions of the experiments. Furthermore, in this region between the two boundaries a portion of the potassium-ion constituent has been concentrated free from the more mobile hydrogen ion present in the original mixture. Though the differences in the mobilities of the two cation constituents of these mixtures are very large, it is probable that the same regulating mechanism is operating in cases where the ion constituents have more nearly the same mobilities, as in mixtures of the rare earths.

Discussion of Results

All experimental values quoted in this paper are the mean of several closely agreeing determinations. The boundary velocities have been corrected for the volume changes as described by Lewis.[20] The apparent equivalent volume was used in making these corrections, this being assumed additive for the mixtures.

Bennewitz, Wagner and Kuchler[18] report measurements by the Hittorf

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[20] Lewis, THIS JOURNAL, 32, 862 (1910).

method on several mixtures at a total concentration of 0.1 normal and at 18°. The only solution where comparison is possible, however, is that which is 0.05 normal to both hydrogen and potassium chlorides. For this solution at 18°, they obtain $T_H = 0.622$, $T_K = 0.124$ and $T_{Cl} = 0.254$. At 25°, the values recorded by the author are $T_H = 0.6198$, $T_K = 0.1242$ and $T_{Cl} = 0.2560$.

With regard to solutions of the pure electrolytes, reference has already been made to the work of MacInnes and co-workers. Denison and Steele,[21] using lithium chloride and potassium acetate as indicators, obtained 0.492 as the cation transference number of 0.1 normal potassium chloride at 18°. Using potassium chloride and iodic acid as indicators for the ions of hydrogen chloride, they obtained a cation transference number of 0.835 for this electrolyte at 0.1 normal and 18°. A comparison of the published values by the moving boundary method is given in Table VIII. The agreement is only fair. The data of this paper fulfil the following conditions, however. (1) They are independent of the potential gradient within wide limits. (2) They are independent of the nature and concentration of the indicator ion within certain limits. (3) They are very reproducible. (4) The sum of the anion and cation transference numbers is very nearly unity.

TABLE VIII

COMPARISON OF THE TRANSFERENCE NUMBERS OF THE SOLUTIONS OF THE PURE SALTS AS OBTAINED BY DIFFERENT INVESTIGATORS

Solution	Dennison and Steele, 18°	MacInnes, et *al.*, 25°	This paper, 25°
0.1 N HCl	0.835	0.8320	0.8305
0.1 N KCl	.492	.4920	.4899

The author wishes to express appreciation to Dr. D. A. MacInnes of these laboratories for the inspiring supervision of this work, to Dr. Theodore Shedlovsky for his cooperation in the determination of the conductivities of the solutions, and to Professor H. P. Cady of the University of Kansas for many helpful suggestions.

Summary

Ion mobility relations and concentration changes on electrolysis in mixtures of hydrogen and potassium chlorides at a total chloride-ion concentration of 0.1 normal have been studied by means of the moving boundary method, using rising boundaries.

Two cation boundaries are formed simultaneously and proceed at different rates. The velocity of the leading boundary yields the mobility of the hydrogen-ion constituent in the mixture. A portion of the less mobile potassium-ion constituent lags behind the hydrogen-ion constituent

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[21] Denison and Steele, *Z. physik. Chem.*, 57, 110 (1907).

and gives rise to a second boundary whose velocity yields information as to the concentration adjustment occurring in the region of the solution which contains pure potassium chloride between the two boundaries. From data on both boundaries it is shown that within this latter region the hydrogen ion has been quantitatively separated from the potassium ion and that the concentration of the potassium chloride residue is accurately determined by the "regulating" function of Kohlrausch,[5] a derivation of which is given.

It is shown experimentally that the mobility of the chloride-ion constituent varies linearly between its slightly different values in 0.1 normal hydrogen chloride and 0.1 normal potassium chloride.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

SURFACE REACTIONS OF ATOMS AND RADICALS. I. A NEW APPROACH TO THE PROBLEM OF SPECIFIC SURFACE ACTION

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The problem of specificity in the action of surfaces is still the outstanding problem of chemical reactivity at solid surfaces. The solution of the problem will contribute materially to the explanation of the varied phenomena grouped under the title of contact catalytic action. Hitherto, discussion of this problem has been confined mainly to the reactions which molecules undergo at various surfaces. Little attention has been paid to the influence of surfaces on reactions of atoms and of radicals. Frequently it has been implicitly assumed that, for reactions between atoms and radicals, a surface only was necessary; little regard has been paid to the influence of the nature of the surface. It is the purpose of the present communication to demonstrate that the surface is of importance in atom–radical reactions as in molecular reactions; that great differences in velocity of such reactions at different surfaces occur, though the actual time of reaction is many orders less than with molecules; that the available data, together with other experimental data presented herewith, indicate a connection between the activity of surfaces in atomic reactions and corresponding processes involving molecules. The evidence already in the literature is diffuse and only assumes important proportions when coordinated. It suggests, however, an extended experimental program of which the first results will be here detailed.

The Recombination of Halogen Atoms at Surfaces.—The specific influence of surface in the rate of recombination of halogen atoms is well illustrated by a recent publication of Senftleben and Germer.[1] In this

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[1] Senftleben and Germer, *Ann. Physik*, **2**, 847 (1929).

work, atomic halogens were produced by illumination with light of wave length within the region of continuous absorption and the existence of atoms was demonstrated by measuring the increase in thermal conductivity of the vapor under illumination. This involved the use of a heated platinum wire which decreased in temperature and resistance when dissociation of the halogen occurred. The platinum wire showed a marked tendency to produce recombination of chlorine atoms; the efficiency of the surface in this respect could be materially diminished by glowing the wire in chlorine, a treatment which undoubtedly covered the surface in part with the metal chloride. In this manner the efficiency of the wire in causing recombination was so far diminished that the effect of illumination in producing dissociation was successfully demonstrated. With bromine the success was less great, it being found difficult to poison the wire so as to prevent recombination of bromine atoms. With iodine a new surface factor became of importance. The glass surface of the containing vessel caused rapid recombination of iodine atoms. To reduce this effect quartz was substituted for glass and proved to have a lower order of efficiency in this respect.

These direct observations may now be supplemented by others, somewhat less direct, involving additional types of surface. The low quantum yields in the photochemical hydrogen–chlorine combination found by Marshall[2] at pressures below 60 mm. could be explained by the influence of the walls on the recombination of atoms taking part in the chain reaction of the secondary processes succeeding the absorption process. This conclusion was more directly confirmed by the work of Trifonoff[3] using vessels of various sizes at low pressures, and by Chapman and Grigg[4] using capillary tubes at normal pressures. This effect of capillaries on atom recombination accounts for the failure of Bodenstein and Taylor[5] and later of Marshall[6] to obtain reaction by illuminating the chlorine alone and passing it directly (but, owing to experimental requirements, through capillaries) to unilluminated hydrogen. No reaction was observed even when the time interval between illumination of the chlorine and admixture with hydrogen was 10^{-4} seconds.

A varying influence of surfaces in this same reaction was demonstrated by Polanyi and Bogdandy[7] who found that when the hydrogen–chlorine combination was initiated by the reaction of chlorine with sodium vapor, $Na + Cl_2 = NaCl + Cl$, the chain length of the hydrogen–chlorine combination was short when a clean glass surface was present, but increased

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[2] Marshall, *J. Phys. Chem.*, 29, 1453 (1925).

[3] Trifonoff, *Z. physik. Chem.*, 3B, 195 (1929).

[4] Chapman and Grigg, *J. Chem. Soc.*, 2426 (1929).

[5] Bodenstein and Taylor, *Z. Elektrochem.*, 22, 202 (1916).

[6] Marshall, *J. Phys. Chem.*, 30, 757 (1926).

[7] Polanyi and Bogdandy, *Z. Elektrochem.*, 33, 554 (1927).

30-fold after the glass surface became covered with sodium chloride. The operating pressure was below 10 mm. of mercury with hydrogen in large excess. In the corresponding experiments with potassium in place of sodium the chain length was shorter, pointing to an increased efficiency of potassium chloride over sodium chloride in the breaking of chains.[8] That the effect of the surface was on the recombination of chlorine atoms was indicated by the authors by reason of experience with the effect of surface on chemiluminescences produced by interaction of sodium and chlorine. Polanyi and Schay[9] found that in the interaction of sodium vapor and chlorine, the chemiluminescent flame was at first short and of weak intensity, gradually becoming stronger and longer as the surface of the vessel became coated with sodium chloride. Since the light-producing reactions are initiated by chlorine atoms, by the reaction sequence (1) $Na + Cl_2 = NaCl + Cl$; (2) $Cl + Na_2 = NaCl' + Na$; (3) $NaCl' + Na = NaCl + Na'$; (4) $Na' = Na + h\nu$, it follows that sodium chloride surfaces are less efficient than glass in terminating the activity of chlorine or sodium atoms. Since chlorine atoms are common to this reaction and the preceding, it indicates that it is the recombination of chlorine atoms which is involved at the two surfaces. This conclusion will be strengthened by our own results on the low efficiency of halide surfaces in the recombination of hydrogen atoms. Polanyi and Bogdandy also indicate that a glass surface which has been browned with sodium vapor is more efficient than clean glass surfaces for these atom recombinations.

The efficiency of glass surfaces in the recombination of chlorine atoms is apparent also in the kinetic analysis of the photochemical formation of phosgene[10] and of the photosensitized oxidation of carbon monoxide in presence of chlorine.[11] These studies show that a change from higher pressures to low pressures causes a change in the reaction kinetics directly associable with the changing influence of the wall in the recombination of chlorine atoms. In ordinary reaction vessels in the photochemical formation of phosgene the change manifests itself below 10 mm. of mercury working pressure. If the glass surface of the reaction vessel per unit volume be greatly increased, the change in kinetics is already revealed at 150-mm. mercury pressure. This points indubitably to the action of the glass wall on the reaction $2Cl = Cl_2$. From the cases cited in the

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[8] There is, however, an untested possibility that the difference in chain length between a potassium chloride and a sodium chloride surface was due to impurities in the gases used. This does not apply to the glass–sodium chloride comparison since this was achieved with a given filling. It is evident that there is nothing improbable in the indicated difference in efficiencies of potassium chloride and sodium chloride for atom recombinations.

[9] Polanyi and Schay, *Z. physik.* Chem., **1B, 30** (1928).

[10] Bodenstein, Lenher and Wagner, ibid., **3B,** 459 (1929).

[11] Schumacher, ibid., 129, 241 (1927), and forthcoming papers.

preceding paragraphs it is evident that the kinetics of these photo-reactions would be modified in entirely different pressure intervals were the walls of the reaction vessels coated with alkali halides. This could readily be made the subject of experimental test.

The Recombination of Hydrogen Atoms at Surfaces.—Wood,[12] in his initial work on the production of hydrogen atoms in discharge tubes, drew attention to the desirability of adding water vapor to the hydrogen used, in order to increase the concentration of hydrogen atoms obtained. Langmuir suggested, as a reason for this, the poisoning action of adsorbed water vapor on the surface activity of the glass walls for recombination. This procedure has since been followed and ice has been employed as the containing surface.[13] Recently von Wartenburg and Schultze[14] have further improved the protection of the glass by coating it with hygroscopic materials. Strong solutions of potassium hydroxide and water glass were useful but sirupy phosphoric acid was very efficient. These authors imply that the efficiency may be due to the film of water which such materials hold on the surface. There may be, however, a specific effect of the materials used.

Bonhoeffer[15] demonstrated a varying capacity of surfaces to effect recombination of hydrogen atoms. Metals were especially efficient and the order of efficiency was that of the metals in respect to activity as hydrogenating catalysts. Bonhoeffer states that, besides metals, many salts and especially oxides also catalyze the recombination. Concerning one oxide, Al_2O_3, cited by Bonhoeffer, we shall give experimental data of our own which are in conflict with this view.

Surface Effects in Explosion and Flame Reactions.—Reactions leading to the development of explosions and flames are now known in many cases to be of the chain reaction type.[16] Whether the chains are atom or radical chains or energy chains is not yet known in individual cases with certainty. In many of these reactions, however, the specific effects of surface are well known. The action of metal-organic compounds as "antiknock" agents in gasoline explosions has been attributed to the effect of the metal particles, produced by thermal dissociation of the compounds, on a chain mechanism produced in the process of gasoline combustion. Egerton[17] seems to favor energy chains but Berl and Winnacker,[18] reasoning from the efficiency of colloidal lead and iron as inhibitors and the

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[12] Wood, *Proc. Roy. Soc.* (London), **102A,** 1 (1923).

[13] Hansen, Ann. *Physik,* 78, 558 (1925).

[14] Von Wartenburg and Schultze, *Z. physik. Chem., 6B,* 261 (1930).

[15] Bonhoeffer, *ibid.,* 113, 199 (1924).

[16] See, for example, Semenoff, *Chem. Rev.,* 6, 347 (1929).

[17] See, for example, Egerton, "Réunion Int. de Chimie Physique," Paris, 1928, p. 489.

[18] Berl and Winnacker, *Z. physik. Chem.,* 145, 161 (1929).

lack of activity of the corresponding dispersed oxides, reject the concept of energy chains and favor some specific chemical reaction (e. g., destruction of peroxide) as the mechanism of inhibition.

Metallic potassium vapor has a marked efficiency as inhibitor in automobile engine combustions and this is to be remembered in conjunction with the well-known use of potassium salts for the prevention of flame at the mouth of cannons firing high explosives.[19] Muraour cites other similar uses of potassium salts.

These latter observations link up with the recent studies of Hinshelwood[20] and of Pease[21] on the influence of surface on the slow combustion of hydrogen and oxygen and hydrocarbons and oxygen. Of especial interest is the observation of Pease that coating the glass surface of the reaction vessel with potassium chloride slows down the rate of reaction approximately 1000-fold. This is not due exclusively to the poisoning of the glass surface for a heterogeneous reaction of combination since an increase of surface by filling with coarse glass powder, either with or without a coating of potassium chloride, slowed down the reaction rate. It is evident that, in the oxidation of hydrogen and hydrocarbons, a surface of potassium chloride is more *efficient* in breaking chains than is a clean glass surface. The contrast between this conclusion and the opposite one reached in the case of chlorine atom recombination is compelling evidence of specificity of surface in chain reactions.

In the hydrogen–oxygen reaction the system is sufficiently simple that experimental evidence may be sought to permit a decision as to the nature of the influence of specific surfaces. Hydrogen atoms, oxygen atoms and hydroxyl radicals are the only atoms or radicals that might be involved if the chain is one involving such species. Spectral evidence indicates that hydrogen and hydroxyl are involved.[22] The behavior of these at surfaces may be studied since, in the hydrogen discharge tube, we have a source of atomic hydrogen and, in the corresponding tube, using water vapor, there is now evidence for the production, together with atomic hydrogen, of hydroxyl (with possibly free oxygen atoms).[23]

Experimental

The method employed consisted in an adaptation of that employed by Bonhoeffer in his study of atomic hydrogen. Thermometers whose bulbs were coated with the material to be studied were inserted in positions B, C and D of the exit tube from a dis-

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[19] Muraour, "Réunion Int. de Chimie Physique," Paris, 1928, p. *502.*

[20] Hinshelwood, *Proc. Roy. Soc. (London),* **118A,** *170, 591 (1928).*

[21] Pease and Chesebro, *Proc. Nat. Acad. Sci., 14,472 (1928);* Pease, THIS *JOURNAL,* 51, *1839* (1929), and forthcoming paper.

[22] Bonhoeffer and Haber, *Z. physik. Chem.,* 136, *263 (1928);* Bonhoeffer and Reichardt, *ibid.,* 139, 75 *(1928).*

[23] Lavin and Stewart, *Proc. Nat. Acad. Sci.,* 15, *829 (1929).*

charge tube operating either with water vapor or hydrogen (Fig. **1).** Since atomic hydrogen was known by spectroscopic observation to persist for longer intervals of time than hydroxyl, positions C and D were ordinarily used for detecting, by temperature rise on the thermometer, any atomic hydrogen recombination. The recombination of hydrogen with hydroxyl was studied at B, position **A** being used, with a clean glass thermometer **bulb,** to determine rise in temperature due to the discharge and also the effect of a clean glass surface on the recombination process. As an index of the active material reaching D, the thermometer bulb in this position was normally coated with metallic silver obtained by atomic hydrogen reduction of silver nitrate, since such a surface was shown by Bonhoeffer to act efficiently as a recombination agent for atomic hydrogen. In order to eliminate differences due to the varying efficiency of the discharge tube, the activities at B and C of the surfaces studied were always compared either with clean glass at **A** or with the silvered surface at D. The results of our experiments are recorded in the accompanying Table **I.** The data given represent a typical selection from a large number of experiments.

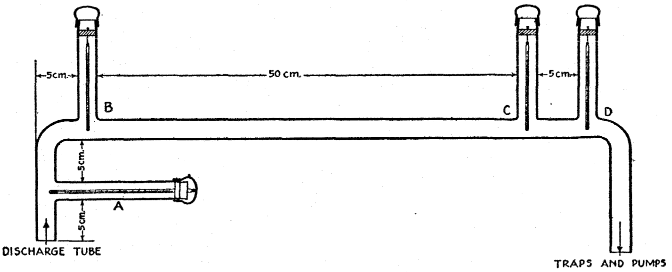

Fig. 1.

TABLE I

RECOMBINATION OF HYDROGEN ATOMS AND HYDROXYL AT VARIOUS SURFACES

Expt.	Nature and position of surface		Gas in discharge tube, ca. 0.5 mm.	Thermometer readings at 1-minute intervals				
1	Clean glass[a]	C	Water	22.5	29	29	29	
	Silver	**D**	Vapor	32.0	52	55	57	
2	KCl	C	Water	27	29	30	30	31
	Silver	**D**	Vapor	32	75	100	111	128
3	KCl	B	Water	32	110	122	123	124
	Silver	**D**	Vapor	31	68	81	87	92
4	Clean glass	**A**	Water	26	27	27	27	28
	KCl	**B**	Vapor	34	118	127	127	127
5	KCl	C	H_2 +	27	28	29	31	32
	Silver	**D**	H_2O at 25°	31	79	106	149	169
6	KCl	B	H_2 +	30	32	34	35	37
	Silver	**D**	H_2O at 25°	27	40	45	48	50
7	KOH	C	Water	29	37	44	54	57
	Silver	**D**	Vapor	31	64	75	82	85
8	KOH[b]	C	Water	29	62	75	83	93
	Silver	**D**	Vapor	27	42	47	50	53
9	K_2CO_3	C	Water	25	31	41	54	102[c]
	Silver	**D**	Vapor	25	41	52	59	69

TABLE I (Concluded)

Bxpt.	Nature and position of surface		Gas in discharge tube, *ca.* 0.5 mm.	Thermometer readings at 1-minute intervals				
10	$ZnO\cdot Cr_2O_3$	C	H_2 +	25	76	94	106	112
	Silver	D	H_2O at 25°	25	29	29	29	28
11	Al_2O_3	C	Water	31	41	46	47	50
	Silver	D	Vapor	37	74	103	135	152
12	Al_2O_3	B	Water	47	95	120	132	
	Silver	D	Vapor	27	48	64	78	..
13	Al_2O_3	C	Water	28	38	42	44	45
	Silver	D	Vapor	34	91	110	138	165
14	Al_2O_3	B	H_2 +	33	57	68	73	79
	Silver	D	H_2O at 5°	30	72	93	100	104
15	Al_2O_3	B	H_2 +	29	82	109	124	132
	Silver	D	H_2O at 34°	30	96	116	125	130
16	Al_2O_3	B	H_2 +	32	93	129	147	159
	Silver	D	H_2O at 54°	32	106	137	147	152
17	Al_2O_3	B	H_2 +	31	102	138	158	169
	Silver	D	H_2O at 74°	31	118	144	153	158
18	Al_2O_3	C	H_2 +	25	32	35	37	38
	$ZnO\cdot Cr_2O_3$	D	H_2O at 25°	25	100	134	152	163

[a] The bulb of a 360° thermometer with opalescent back and etched scale constituted the glass surface. It was carefully washed in distilled water and dried with a soft cloth.

[b] KOH covered thermometer allowed to stand for one day in air and then again tried in Expt. 8.

[c] Two-minute interval.

Discussion of Experimental Data

It is apparent from Expts. 1, 2, 5 and 6 that neither a clean glass surface nor a potassium chloride surface has any marked efficiency in the recombination of hydrogen atoms either from water vapor at position C or from moist hydrogen at positions A or B. In marked contrast to this is the efficiency of potassium chloride as a reaction surface at position B when water vapor is passed through the discharge tube (Expts. 3 and 4). In this it is markedly superior to a clean glass surface at A (Expt. 4). We associate this efficiency with a recombination of hydrogen and hydroxyl since spectroscopic evidence shows marked concentrations of the latter at B and also for reasons indicated in the subsequent discussion of alumina.

Potassium hydroxide shows a more pronounced efficiency for atomic hydrogen recombination than does the chloride (Expts. 7 and 8 compared with Expt. 2). On standing in the air the potassium hydroxide appeared to improve in efficiency (Expt. 8). We, therefore, were led to try potassium carbonate and thus found it also to have good efficiency in the combination of atomic hydrogen (Expt. 9). When a surface shows marked activity in atomic hydrogen recombination at C, its test at B for the H–OH combination is useless since the present method of test does not distinguish between the two reactions, and at B there is always a higher concentration of hydrogen atoms than at C under given discharge tube conditions.

The specific action of surfaces, thus found for the two reactions, suggested a correlation with the specific behavior of surfaces in similar reactions involving molecules. Thus, the combination of atomic hydrogen and hydroxyl is analogous to the removal of water from organic molecules by means of dehydration catalysts. The recombination of atomic hydrogen is analogous to the removal of hydrogen from organic compounds by dehydrogenation catalysts. It seemed probable, therefore, that a purely dehydration catalyst might promote H–OH recombination without affecting the H–H reaction, while a purely dehydrogenation catalyst might secure the H–H recombination. To test this, we chose alumina as a dehydration catalyst and the now well-known mixture of zinc and chromium oxides (used in methanol synthesis) as a typical oxide dehydrogenation catalyst. The correlation of hydrogen atom recombination on metals with the catalytic activity of the latter has already been indicated by Bonhoeffer.[15] Our expectations were completely realized. It is evident that alumina has high efficiency in position B and low efficiency at position C (cf. Expts. 11, 12 and 13). Experiment 13 was especially conclusive since it immediately succeeded Expt. 12 in which the high activity at B was realized. Nevertheless, in Expt. 13 at C, only the activity associated with a small amount of residual water vapor is to be noted. Its inertness toward atomic hydrogen is also manifest in Expt. 18, where a zinc–chromium oxide surface immediately beyond it revealed a high residual concentration of atomic hydrogen.

We wish also to record one other observation with alumina which bears upon the problem of its surface activity. The oxide was prepared from the precipitated hydroxide which was dried after it had been placed on the thermometer bulb. The product displayed no activity at all in either position B or C until it had been dehydrated by heating in an electric furnace to 300°. A treatment of this kind at 250° was insufficient to activate the surface. This points to a poisoning of the oxide surface by adsorbed water.

It appeared necessary, in view of the observation already recorded by Bonhoeffer as to the efficiency of alumina in atomic hydrogen recombination, to ascertain to what factor Bonhoeffer's observation was due. We accordingly tested alumina at position B, the discharge tube operating with a stream of hydrogen which had been bubbled through water maintained at various temperatures. A perusal of the selection of our results given (Expts. 14–17) will indicate that the temperature rise obtained is dependent on the concentration of water vapor in the gas stream. We suggest, therefore, that Bonhoeffer's results with alumina were due to the hydroxyl content of his atomic hydrogen.

The efficiency of zinc–chromium oxide for the atomic hydrogen recombination in comparison even with silver is shown in Expt. 10 as well as in the Expt. 18 already quoted.

We wish also to record the observation that the active combination of the atoms and radicals in question is associated in many instances with the production of distinctive chemiluminescences at the reaction surfaces. With potassium chloride and water vapor in the discharge, the glow was purple; with potassium hydroxide and potassium carbonate a blue-green. With alumina one obtains also a purple glow. With zinc–chromium oxide and on the silvered thermometer there was no observable light production. We propose to investigate these phenomena in detail later.

Our experiments have demonstrated that the specificity of behavior of dehydration and dehydrogenation catalysts is associable with their activity in producing the recombination of H–OH and H–H, respectively. We plan a further series of investigations to ascertain the factors controlling the activity of surfaces in these simple reaction processes and hope thence to derive the explanation of specific surface action in these molecular processes.[24]

Summary

1. It has been demonstrated that the nature of the surface is of fundamental importance in determining the velocity of atom–radical reactions.
2. Potassium chloride is more efficient than clean glass in H–OH recombination. It is less efficient than clean glass in Cl–Cl recombination. Alumina is very efficient in the H–OH reaction.
3. Potassium chloride and alumina are inefficient in H–H recombination. Potassium hydroxide and carbonate, and especially zinc–chromium oxide, are efficient agents for this reaction as are also metal surfaces.
4. Active recombination of atoms and radicals is associated with the production of distinctive chemiluminescences at several of the surfaces.
5. A correlation of the activity of surfaces in atomic reactions with similar processes involving molecules has been given and the importance of this in the problem of specific surface activity has been indicated.

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[24] It is evident that analogous to this specificity of surface in atom–radical reactions, there should exist specific third-body action in homogeneous systems. Such specificity is fundamental in the kinetics of such reactions, has not been emphasized and yet apparently exists in reactions already studied.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY AND FROM THE DEPARTMENT OF PHYSICS, JOHNS HOPKINS UNIVERSITY]

THE DIPOLE MOMENTS OF THE DISUBSTITUTED BENZENES

BY HUGH M. SMALLWOOD AND K. F. HERZFELD

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Recent measurements of the dipole moments of organic molecules[1] have shown that the symmetrical hydrocarbons have no electric moment and that their mono-derivatives possess moments varying with the nature of the substituent group. It has further been shown, in accordance with a prediction of J. J. Thomson,[2] that the moment of a disubstituted hydrocarbon may be calculated, in certain cases, from the assumption that it is the vector sum of individual moments characteristic of the substituent groups and that these group moments are directed along the conventional valence bonds joining the substituents to the hydrocarbon residue. Thus, for example, if it be supposed that the carbon atoms of the benzene nucleus are situated at the corners of a regular hexagon, the moment of a disubstituted benzene may be calculated from the law of cosines

$$M = \sqrt{m_1^2 + m_2^2 + 2\, m_1 m_2 \cos \beta} \tag{1}$$

where M is the resultant moment of the molecule, m_1 and m_2 are the individual group moments, and β is the angle between m_1 and m_2. If the substituent groups are in the ortho position, @ = 60°; if in the meta position, $\beta = 120°$; and if in the para position, $\beta = 180°$. It has been found that the groups —Cl, —Br, —I, —CH_3 and —NO_2 follow this rule approximately, but that the experimental data for compounds containing —OH, —NH_2 and —O— do not obey it even qualitatively. The discrepancies shown by the last named groups have been explained by the postulate that the resultant group moment does not lie along the valence bond of the usual structural formula. This seems quite probable since analysis of the infra-red spectra of H_2O and of NH_3 indicates a triangular model for the former and a pyramidal model for the latter. If this structure is preserved in the —OH and —NH_2 groups, it follows that these groups are unsymmetrical about the line joining the centers of the carbon and oxygen or carbon and nitrogen atoms. They may, therefore, be expected to exhibit a moment in some direction other than that of the line of centers. On the other hand, the groups which do follow the rule of vector additivity are symmetrical about the line of centers.

The moments calculated for those compounds which do obey the rule, however, show systematic variations from the experimental values. Thus

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[1] For reviews of this subject and references to the literature *see* C. P. Smyth, *Chem. Rev.*, 6, 549 (1929); I. Estermann, *Ergebnisse Exak. Naturwiss.*, 8, 258 (1929). H. Sack, *ibid.*, p. 307.

[2] J. J. Thomson, *Phil. Mag.*, 46, 513 (1923).

the calculated moments of compounds of the type *o*-$C_6H_4X_2$ are from 10 to 30% higher than the experimental values. Höjendahl[3] has explained this by pointing out that the simple theory takes no account of interaction between the two dipoles. Such interaction might consist of either or both of two effects. In the first place there is a repulsive force between two dipoles in the ortho position which tends to force the dipoles apart, that is, to increase β of Equation 1. It is therefore possible to use β as an adjustable constant in order to bring the calculated value of M into agreement with the observed. In the second place, the dipoles may affect each other by induction. Since these molecules are not rigid and since each group is subjected to an electric force exerted by the other, dipole moments will be induced in each group in such a direction as to lessen the resultant moment. It is the purpose of the present paper to calculate the resultant moments of the disubstituted benzenes from the individual moments of the substituent groups, assuming that the group moments are directed along the valence bonds but taking into account the moments due to induction.

The dipole moment induced in any substituent as a result of an electric intensity E is given by the expression[4,5]

$$\mathbf{m}_i = \alpha\mathbf{E} \tag{2}$$

where α is the deformability of the substituent group. In the present case E is the force exerted by the dipole of the other constituent. If the dipole m exerting the force E is situated at the origin of a set of plane polar coordinates, the horizontal and vertical components of $\mathbf{E}$(E_x and E_y) at the point (r), are given by the equations.[6]

Equations 3 then follow since

$$E_x = -\frac{\partial\varphi}{\partial x} \text{ and } E_y = -\frac{\partial\varphi}{\partial y}$$

$$\left.\begin{aligned} E_x &= \frac{\xi}{r^3}\,(3\cos^2 6 - 1) + \frac{3\eta}{r}\sin 6 \cos 6 \\ E_y &= \frac{3\xi}{r^3}\sin 6\cos 6 + \frac{\eta}{r^3}\,(3\sin^2 6 - 1) \end{aligned}\right\} \qquad (3$$

where ξ and η are the horizontal and vertical components of m.

In order to calculate the resultant moment, M, of the molecule, it is

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[3] K. Höjendahl, "Dissertation," Copenhagen, **1928**; Physik. Z., **30**, 391 (1929); *cf.* also Estermann, ref. 8.

[4] P. Debye, "Polar Molecules," The Chemical Catalog Co., Inc., New York, **1929.**

[5] Throughout this article vector quantities will be indicated by bold face type.

[6] Cf. Jeans, "Electricity and Magnetism," Cambridge, **1925**, p. 50. The potential, φ, at a point (x, y) due to charges + e at (a, b) and $-e$ at $(-a, -b)$ is

$$\varphi = \frac{e}{\{(x-a)^2 + (y-b)^2\}^{1/2}} - \frac{e}{\{(x+a)^2 + (y+b)^2\}^{1/2}}$$

Upon expanding this expression and neglecting squared and higher terms, it is found that

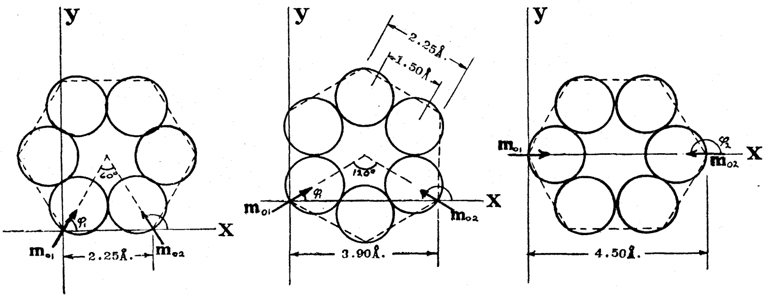
$$\varphi = \frac{2e(ax+by)}{(x^2+y^2)^{3/2}} = \frac{\xi x + \eta y}{(x^2+y^2)^{3/2}}$$

necessary to take into account the moments induced in the four unsubstituted —CH groups. These moments may be represented by the symbol $\mathbf{m}_i'$. $\mathbf{M}$ is then given by the expression

$$\mathbf{M} = \mathbf{m}_{o1} + \mathbf{m}_{i1} + \mathbf{m}_{o2} + \mathbf{m}_{i2} + \mathbf{m}_i' \tag{4}$$

where $\mathbf{m}_{o1}$ and $\mathbf{m}_{o2}$ are the original moments of groups 1 and 2, $\mathbf{m}_{i1}$ and $\mathbf{m}_{i2}$ the corresponding induced moments and $\mathbf{m}_i'$ the resultant moment induced in the —CH groups.

In order to apply these equations it is necessary to know the dimensions of the molecules involved. Although x-ray diffraction data on crystals indicate a tilted model for the benzene nucleus,[7] chemical evidence together with the small electric moment of symmetrical tri-derivatives of benzene may be cited in favor of a plane model for the benzene ring in substituted compounds.[8] The question cannot be regarded as settled at present.



Ortho Meta Para

Fig. 1.—Benzene nuclei and positions of dipoles of substituent groups in *ortho,* meta and para compounds.

Since, however, the differences in the dimensions of the two models are too slight to affect the present calculations, the plane model has been chosen for the sake of simplicity. The radius of the carbon atom has been taken equal to 0.75 Å.,[7] the value obtained from crystal structure data. The centers of the six carbon atoms are therefore assumed to lie on the corners of a regular hexagon of side equal to 1.50 Å.

In order to locate the position of the dipoles associated with the substituent groups, they are assumed to be situated at the circumference of the carbon atoms to which the particular groups are attached, and to be directed along a diagonal of the hexagon. Thus in all the compounds the group moments are assumed to be situated at the corners of a regular hexagon of side equal to 2.25 Å. (Fig. 1). Using this model it follows that the distance between the dipoles of the two substituents is 2.25,

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[7] W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," London, 1924, p. 229, ff.

[8] I. Estermann, *Leipziger Vortrage,* p. 34 (1929).

3.90 or 4.50 Å., according to whether the substituents are in the ortho, meta or para position.

It is next necessary to obtain numerical values for ***a***. This quantity is related to the atomic refraction ***R*** by the equation

$$\alpha = 3R/4\pi N_A \tag{5}$$

where N_A is the Avogadro number per mole. Since ***R*** varies with the wave length of the light used in its determination, the values must be extrapolated to infinite wave length. This has been done, using the assumption that the curve of R against A becomes parallel to the λ axis in the region of the far infra-red. The values so obtained are tabulated in the first column of Table I. The quantity under consideration, however, is more a property of the bond between two atoms than of a single atom. It has, therefore, seemed advisable to use the octet refractions of the various groups in the calculations of ***a***. The octet refraction was introduced by Smyth[9] and defined by him as

$$R_{oct} = R_{at} + {}^1/_4 R_c \tag{6}$$

Here R_{at} is the usual atomic refraction and R_c the atomic refraction of carbon. The values of R_{oct} are tabulated in the second column of Table I and those of a in the third column. This use of R_{oct} instead of R_{at} involves such a slight change in α that the final results are not appreciably affected.

TABLE I

Group	R_{at}[a]	R_{oct}	$\alpha \times 10^{24}$	$m_c \times 10^{18}$		
—H	1.065	1 661[b]	0.654	0		
—Cl	5.789	6.38	2.51	−1.53"	−1.55[d]	−1.64"
—Br	8.636	9.23	3.63	−1.50[f]	−1.56"	
—I	13.297	13.89	5.46	−1.25'		
—CH_3	5.581	6.18	2.45	+0.43[e,f,h]		
—NO_2	6.39	6.99	2.75	−3.75"	−3.90[f]	

[a] Data from Landolt-Börnstein, "Physikalisch-Chemischen Tabellen," 5th **ed.**, Berlin, 1923, p. *985*, extrapolated to infinite wave length. [b] This is a "bond refraction" rather than an octet refraction. [c] C. P. Smyth, S. O. Morgan and J. C. Boyce, THIS JOURNAL, *50, 1536 (1928).* [d] J. W. Williams and E. F. Ogg, *ibid., 50, 94 (1928).* [e] K. Höjendahl, Ref. 3. [f] J. W. Williams, *Physik. Z.*, 29, *174, 204, 271, 683 (1928);* THIS JOURNAL, *50, 2350 (1928).* [g] P. Walden and O. Werner, *Z. physik. Chem., 2B, 10 (1929).* [h] C. P. Smyth and S. O. Morgan, THIS JOURNAL, *49,1030 (1927).*

The experimental values of the moments of the monosubstituted compounds cannot be identified with the $\mathbf{m}_o$'s of Equation 4 since the former are the resultants of the latter and the moments induced in the five unsubstituted —CH groups. In order to calculate the actual group moment, m,, from the experimental value m, consider a set of axes oriented with respect to the benzene ring as in Fig. 2. Since the molecule is symmetrical about the x-axis,

$$\Sigma\eta_i = 0$$

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[9] Smyth, *Phil.* Mag., *50,361 (1925); cf* also Fajans and Knorr, ***Ber.***, *59,249 (1926).*

Then

$$m_e = m_o + \Sigma\xi_i$$
$$= m_o + 2\xi_{i2} + 2\xi_{i3} + \xi_{i4}$$

where ξ_{i2}, etc., are the x-components of the moments induced in the second —CH group and so on. Substituting from Equations 3 it follows that

$$\mathbf{m}_e = 1.013\mathbf{m}_o \qquad (7)$$

if it be assumed that the fields of the induced moments are too small to produce an appreciable effect upon $\mathbf{m}_o$.

The foregoing assumption is valid only because the induced moments are small as a result of the small deformability of the —CH group. In calculating the moments induced in the substituent groups themselves, in the case of the disubstituted compounds, it is necessary to take into account the fields of the induced moments as well as those of the original moments. This can be done by substituting in the equations

$$\xi = {}_{40} + \xi_i \qquad (8)$$
$$\eta = \eta_o + \eta_i$$

where ξ_o, η_o are the components of the original group moment and ξ_i, η_i the components of the moment induced in that group by the second dipole.

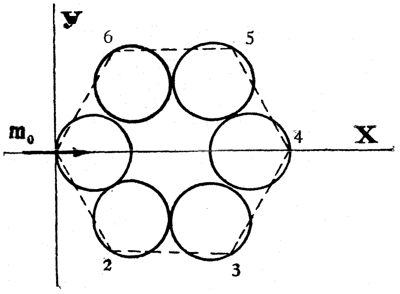

Fig. 2. .

Finally, it is necessary to calculate $\mathbf{m}_i'$, the moments induced in the unsubstituted —CH groups. This calculation is quite analogous to that leading to Equation 7. In this case, however, as well as in the final calculation, it is advantageous to choose the coördinate axes so that the substituent groups both lie on the x-axis (Fig. 1). Assuming, as before, that the moments induced in the —CH groups are too small to affect each other or the inducing groups, the total components of the former are found to be

$$\xi_i' = A'(\xi_1 + \xi_2) + A''(\eta_1 - \eta_2)$$
$$\eta_i' = B'(\xi_1 - \xi_2) + B''(\eta_1 + \eta_2) \qquad (9)$$

Here the subscripts 1,2 refer to groups 1,2. The ξ, η are the components of the total moments of the substituent groups. The *A's* and *B's* are numerical coefficients depending on the deformability of the —CH group and on the dimensions of the molecule. Their values are

	Ortho	Meta	Para
A'	−0.01339	+0.0206	+0.001083
A''	− .0511	− .0511	0
B'	− .0511	− .0511	0
B''	+ .1001	+ .1125	0

The resultant moment of the molecule may now be obtained by substituting Equations 2, 3, 8 and 9 in Equation 4. The result is

$$M^2 = \left[(1 + A')\left(\frac{(1 + 2a_2)\xi_{o1} + (1 + 2a_1)\xi_{o2}}{1 - 4a_1a_2}\right) + A''\left(\frac{(1 + a_2)\eta_{o1} - (1 + a_1)\eta_{o2}}{1 - a_1a_2}\right)\right]^2 +$$

$$\left[(1 + B'')\left(\frac{(1 - a_2)\eta_{o1} + (1 - a_1)\eta_{o2}}{1 - a_1a_2}\right) + B'\left(\frac{(1 - 2a_2)\xi_{o1} - (1 - 2a_1)\xi_{o2}}{1 - 4a_1a_2}\right)\right]^2 \qquad (10)$$

where a_1 and a_2 are equal to α_1/r^3 and α_2/r^3, respectively. ξ_{o1} and η_{o1} are obtained from Fig. *1* and Equation *7*.

$$\xi_{o1} = \frac{\cos \varphi_1}{1.013}\, m_{e1} \qquad \eta_{o1} = \frac{\sin \varphi_1}{1.013}\, m_{e1} \qquad (11)$$

Similar equations give ξ_{o2} and η_{o2}. It should be noted that Equation *10* contains no adjustable constants.

Upon selecting values of m_e with which to test Equation *10* it becomes apparent that the accuracy of the data given in the literature leaves much to be desired. Since the experimental data vary with the method and apparatus used, the relative agreement is better than the absolute. It has therefore seemed advisable, wherever possible, to use in the calculation of M that value of m_e determined by the same experimenter who measured M. Although in general better than the absolute, the relative agreement is not good in all cases. For example, the values obtained by Williams and by Hojendahl for the moment of *o*-dinitrobenzene, *6.05* $\times 10^{-18}$ and *6.00* $\times 10^{-18}$, respectively, are in good agreement, but their results for nitrobenzene, *3.90* $\times 10^{-18}$ and *3.75* $\times 10^{-18}$ show greater divergence.

The values of m_e used in the calculation are tabulated in the last column of Table I. The plus and minus signs indicate that some of the dipoles point toward and others away from the center of the ring. The assignment of sign to any one group is quite arbitrary. Once it is fixed, however, the signs of the other groups are definitely established.

The results of the calculations are summarized in Table II. Here the names of the compounds are given in the first column, the experimental

TABLE II

DIPOLE MOMENTS $\times 10^{18}$

Compound	*M, obs.*	*M, calcd., approx.*	Δ_1	*M, calcd., Eq. 10*	Δ_2	*M'*	Δ_3	*Remarks*
o-$C_6H_4Cl_2$	2.25[a]	2.68	−0.33	2.30	−0.05	2.16	+0.09	$m_e = 1.53$
m-$C_6H_4Cl_2$	1.48[a]	1.55	− .07	1.48	0	1.44	+ .04	$m_e = 1.53$
p-$C_6H_4Cl_2$	0[a]	0		0		0		
o-$C_6H_4Br_2$	1.87[b]	2.60	− .73	2.09	− .22	1.94	− .05	$m_e = 1.50$
m-$C_6H_4Br_2$	1.55[b]	1.50	+ .05	1.43	+ .12	1.37	+ .18	$m_e = 1.50$
p-$C_6H_4Br_2$	0[b]	0		0		0		
o-$C_6H_4I_2$	1.63[c]	2.17	− .54	1.56	+ .07	1.43	+ .20	$m_e = 1.25$
m-$C_6H_4I_2$	1.01[c]	1.25	− .24	1.14	− .13	1.10	− .09	$m_e = 1.25$
p-$C_6H_4I_2$	..	0		0		0		

TABLE II (Concluded)

Ccmpound	M, obs.	M calcd., approx.	Δ_1	M calcd., Eq. 10	Δ_2	M'	Δ_3	Remarks
o-$C_6H_4(CH_3)_2$	0.58[d]	0.75	−0.17	0.65	−0.07	0.61	−0.03	$m_e = 0.43$
m-$C_6H_4(CH_3)_2$	0.46[e]	0.43	+ .03	0.42	+ .04	0.41	+ .05	$m_e = 0.43$
p-$C_6H_4(CH_3)_2$	0[d]	0		0		0		
o-$C_6H_4(NO_2)_2$	6.05[d]	6.75	− .70	5.80	+ .25	5.39	+ .66	$m_e = 3.90$
m-$C_6H_4(NO_2)_2$	3.81[d]	3.90	− .09	3.77	+ .04	3.68	+ .13	$m_e = 3.90$
p-$C_6H_4(NO_2)_2$	0[d]	0		0		0		
p-C_6H_4ClBr	0.1[d]	0.05	+ .05	0.09	+ .01	0.09	+ .01	$m_{e1} = 1.55$ $m_{e2} = 1.50$
o-C_6H_4BrI	1.73[b]	2.38	− .65	2.09	− .36	1.78	− .05	$m_{e1} = 1.50$ $m_{e2} = 1.25$
m-C_6H_4BrI	1.14[b]	1.39	− .25	1.34	− .20	1.32	− .18	$m_{e1} = 1.50$ $m_{e2} = 1.25$
p-C_6H_4BrI	0.49[b]	0.25	+ .24	0.33	+ .16	0.33	+ .16	$m_{e1} = 1.50$ $m_{e2} = 1.25$
o-$C_6H_4ClNO_2$	4.25[f]	4.78	− .53	4.39	− .14	4.16	+ .09	$m_{e1} = 1.64$ $m_{e2} = 3.75$
m-$C_6H_4ClNO_2$	3.38[f]	3.26	+ .12	3.30	+ .08	3.28	+ .10	$m_{e1} = 1.64$ $m_{e2} = 3.75$
p-$C_6H_4ClNO_2$	2.55'	2.11	+ .44	2.21	+ .34	2.21	+ .34	$m_{e1} = 1.64$ $m_{e2} = 3.75$
p-$C_6H_4BrNO_2$	2.53[f]	2.19	+ .34	2.37	+ .16	2.37	+ .16	$m_{e1} = 1.56$ $m_{e2} = 3.75$
o-$C_6H_4CH_3Cl$	1.39[b]	1.38	+ .01	1.81	− .42	1.65	− .26	$m_{e1} = 0.43$ $m_{e2} = 1.55$
m-$C_6H_4CH_3Cl$	1.60[b]	1.81	− .21	1.91	− .31	1.93	− .33	$m_{e1} = 0.43$ $m_{e2} = 1.55$
p-$C_6H_4CH_3Cl$	1.74[b]	1.98	− .24	2.06	− .32	2.06	− .32	$m_{e1} = 0.43$ $m_{e2} = 1.55$
o-$C_6H_4CH_3NO_2$	3.75[d]	3.70	+ .05	4.45	− .70	3.98	− .23	$m_{e1} = 0.43$ $m_{e2} = 3.90$
m-$C_6H_4CH_3NO_2$	4.20[d]	4.13	+ .07	4.35	− .15	4.23	− .03	$m_{e1} = 0.43$ $m_{e2} = 3.90$
p-$C_6H_4CH_3NO_2$	4.5[d]	4.33	+ .17	4.51	− .01	4.51	− .01	$m_{e1} = 0.43$ $m_{e2} = 3.90$

[a] *Smyth, Morgan and* Boyce, *loc. cit.* [b] *Walden and Werner, loc. cit.* [c] *J.* Errera, *"Polarisation Dielectrique," Paris, 1928.* [d] *Williams, loc. cit.* [e] *Smyth and Morgan, loc. cit.* [f] Höjendahl, *loc. cit.*

values of M in the second and, in the third, the values of M calculated from the approximate equation (1). In the fourth column are listed the differences between the observed values of M and the approximate calculated values (Δ_1). The values of M calculated from Equation 10 are given in the fifth column. In the sixth are listed the differences between the observed values and those calculated taking into account the effect of induction (Δ_2). The figures listed under the headings M' and Δ_3 will be discussed below. In the last column, headed "Remarks," are tabulated the values of m_e used in the calculations.

Inspection of Table II shows that all the values calculated from the assumption of interaction by induction, except for two groups of compounds, are nearer to the observed values than are those calculated from the approximate equation (1). For most compounds the agreement is within the experimental error. The cases in which the agreement is not good will be referred to later.

The Referee to whom this paper was referred, in order to pass upon its suitability for publication, criticized the method of calculation on the grounds that changes in the moments of the —C—C— bonds of the benzene nucleus should have been taken into account, since the changes in the —CH bonds are considered. We wish to express our indebtedness to him for raising this point. The omission was due to the fact that the effect of the —CH bonds is altered by the entrance of the second substituent group since in the disubstituted compound there is one less —CH bond than in the monosubstituted. The number of —C—C— bonds is the same in both types of compounds. Hence it seemed permissible to neglect the latter. For the sake of completeness, however, the calculations have been repeated taking into account the changes in the moments of the —C—C— bonds. This extension of the calculation merely involves using different values for the proportionality constant of Equation 7 and for the constants A', A'', B' and B'' of Equations 9. To arrive at numerical values for these constants it was assumed that the induced moments in question are located at the "points of contact" of the carbon atoms. α_{cc} was taken equal to 0.984×10^{-24} since

$$R_{cc} = \frac{1}{6}\left(R_{C_6H_6} - 6R_{CH}\right)$$

The constant of Equation 7 then turns out to be 2.38 instead of 1.013 and the others are

	Ortho	Meta	Para
A'	0.1159	0.939	1.348
A''	.712	.712	0
B'	.712	.712	0
B''	.939	.1159	0

The results obtained with the use of these values are listed in Table II under the headings M' and Δ_3. In most cases the values of M' do not differ essentially from those for $M_{\text{calcd.}}$ previously obtained, as is to be expected. In general the agreement between calculated and observed is slightly better than before. The improvement is greatest for the chlorotoluenes and o-nitrotoluene, but for these compounds the agreement still is not as good as might be desired. Moreover, consideration of the —C—C—

bonds makes the agreement in the cases of o-dinitrobenzene definitely worse. It is difficult to explain these discrepancies. The inconsistency of the experimental data for nitrobenzene has already been pointed out. Perhaps in the chlorotoluenes and o-nitrotoluene there is some other type of interaction between the substituent groups. It is unfortunate that there are available no other measurements upon compounds of this type, namely, compounds in which one dipole is directed toward and the other away from the center of the ring.

One further point must be considered in connection with calculations of this type. This is that, under sufficiently great electric intensity, Equation 2 is no longer valid since α must eventually decrease as E increases. The reality of this effect may be observed in Debye's[10] calculation of the moment of HCl. Furthermore, we have attempted to apply the methods of this paper to the derivatives of methane. In this case the correction term is again much too large, indicating that the region of validity of Equation 2 has been exceeded. Apparently the present methods cannot be employed when the distance from the inducing dipole is much less than 2 . On taking into account the —C—C— bonds in the above calculations, however, it is necessary to consider distances considerably smaller than this. That the results are satisfactory is only due to the fact, previously pointed out, that the effect of the —C—C— bonds very nearly cancels out of the resultant moment.

The determining factor in the correction for induction is the distance between the dipoles, since this enters to the third power. The results show that a correction of this type leads to concordant results only when the dipoles are assumed to be situated at the circumference of the carbon atoms. If the dipoles are assumed to be at the center of the substituent group, the effect considered in this paper is negligible. If they are assumed to be at the centers of the carbon atoms, this correction is far too large.

Summary

The calculated dipole moments of the disubstituted benzenes have been corrected for the effect of the mutual induction of the dipoles. The results show that, in order that a correction of this kind be successful, the dipoles must be assumed to be located on the circumferences of the carbon atoms, that is, at the conventional valence bond.

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[10] P. Debye, Ref 4. p 62.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

AZIDO-DITHIOCARBONIC ACID. V. ALKYL AND ACYL DERIVATIVES[1,2,3]

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WITH MICROSCOPICAL STUDIES BY C. W. MASON

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The marked photosensitivity of certain compounds of azido-dithiocarbonic acid with strongly electropositive elements or radicals, particularly the cesium, rubidium and tetramethylammonium salts, has been attributed[1c,1d] to a tendency on the part of these substances to undergo a reversible, superficial photolysis which results in the liberation, in situ, of certain metallic atoms or radicals in the crystal lattice. The hypothesis thus formulated serves also to explain the action of light in accelerating the decomposition of the solid inorganic azido-dithiocarbonates thus far studied. Discharge of the anions yields free azido-carbondisulfide, $SCSN_3$, which is known[2g] to undergo spontaneous thermal decomposition at ordinary temperatures into thiocyanogen, sulfur and nitrogen.

Photolytic action of the type thus assumed to take place during the illumination of the inorganic salts already investigated, all of which are believed to crystallize in the form of ionized lattices, could scarcely be expected to occur in the case of organic derivatives of azido-dithiocarbonic acid, which would, in all probability, in the solid state, take the form of molecular lattices. An important incentive to the preparation and study of these derivatives, none of which has yet been described, is therefore furnished by the possibility of investigating compounds of this type from the viewpoint of the hypothesis under consideration.

A second incentive is afforded by the desire to investigate the influence of various substituents for hydrogen upon the velocity of thermal decomposition of azido-dithiocarbonic acid,[2a] and upon the nature of the products of such decomposition. It is by no means a foregone conclusion

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[1] For the earlier articles of this series see (a) Smith and Wilcoxon with Browne, THIS JOURNAL, **45,** 2604 (1923); (b) Browne and Smith, *ibid.*, **47,** 2698 (1925); (c) Browne and Audrieth, *ibid.*, **49,** 917 (1927); (d) Audrieth, Smith and Browne, *ibid.*, 49,2129 (1927).

[2] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present publication is Article 4 under Heckscher Grant No. 60. For Articles 1, 2 and 3, see (a) *ibid.*, **45,** 2604 (1923); (b) **47,** 1916 (1925); (c) **49,** 2129 (1927). For articles 1, 2, 3 and 4 under Heckscher Grant No. 4, see (d) *ibid.*, **44,** 2106 (1922); (e) 44, 2116 (1922); (f) **44,** 2315 (1922); (g) **45,** 2541 (1923).

[3] This paper was presented at the St. Louis Meeting of the American Chemical Society in April, 1928. Manuscript received April 9, 1929, but withheld from publication by the author.

that organic derivatives of various types should decompose in a manner strictly analogous to that characteristic of the inorganic salts. It is entirely possible, for example, that in certain cases normal thiocyanates, and in others isothiocyanates, might be obtained as products of thermal decomposition.

In the present article are described the methyl, benzyl, benzohydryl, triphenylmethyl, benzoyl and *p*-bromobenzoyl derivatives of azido-dithiocarbonic acid.

Preparation.—Attempts to obtain alkyl and aryl azido-dithiocarbonates by direct condensation of the organic azides with carbon disulfide by a method analogous to that used in preparing the inorganic derivatives[2] did not prove successful. Formation of the azido-dithiocarbonates evidently involves the transfer of electrons from the azide ion to a molecule of carbon disulfide, or, more specifically, to one of the sulfur atoms of the disulfide, with consequent condensation of the two radicals: $N_3^- + CS_2 = SCSN_3^-$. Since the organic azides are not dissociated to an appreciable degree, the electronic transfer does not take place.

The general method finally adopted for the preparation of the compounds to be described involves the interaction, in acetone, of the alkyl or acyl halide and sodium azido-dithiocarbonate, in accordance with the equation:

$$RCl + NaSCSN_3 = NaCl + RSCSN_3$$

With the bromides, with triphenylmethyl chloride and with the acyl chlorides the reaction proceeds rather rapidly at room temperature. In the case of less reactive chlorides, the use of higher temperatures is precluded by the instability of the products. The precipitated metallic halide is removed by filtration, and if the product is but slightly soluble in acetone, the precipitate is treated with chloroform to extract the azido-dithiocarbonate.

General Properties.—All of the organic azido-dithiocarbonates studied were obtained as white, crystalline compounds which undergo at room temperature a slow spontaneous decomposition, with ultimate quantitative formation of the corresponding thiocyanate or isothiocyanate,[4] sulfur and nitrogen:

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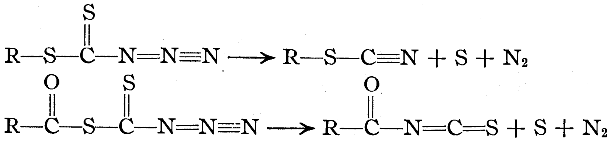
[4] The *normal* thiocyanates were invariably obtained as decomposition products of the alkyl azido-dithiocarbonates. In view of the circumstance that no normal acyl thiocyanate has as yet been isolated, it is not surprising that isothiocyanates, only, have been obtained by decomposition of the acyl derivatives. It is entirely possible, however, that the normal thiocyanate is in each case formed at first, as an intermediate product, but that, as suggested by Wheeler and Merriam[5] for the case of esters in which "the group R is strongly negative the product immediately undergoes a molecular rearrangement into the form RNCS (when R is the group C_6H_5CO-, etc.)."

[5] Wheeler and Merriam, THIS JOURNAL, **23**, 285 (1901).



$$R—S—\overset{\overset{S}{\|}}{C}—N=N\equiv N \longrightarrow R—S—C\equiv N + S + N_2$$

$$R—\overset{\overset{O}{\|}}{C}—S—\overset{\overset{S}{\|}}{C}—N=N\equiv N \longrightarrow R—\overset{\overset{O}{\|}}{C}—N=C=S + S + N_2$$

The velocity of this decomposition is sufficiently retarded at low temperatures to permit the storage of samples of the products at 0° for several weeks without appreciable deterioration.

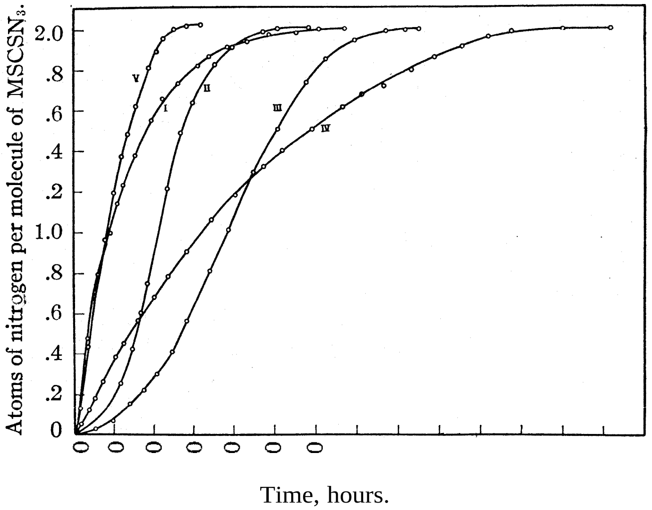


Fig. 1.—Nitrometric decomposition of derivatives of azido-dithiocarbonic acid at 40°. I, CH_3SCSN_3; II, $(C_6H_5)_2CHSCSN_3$; III, $C_6H_5CH_2SCSN_3$; IV, $(C_6H_5)_3CSCSN_3$; V, $C_6H_5COSCSN_3$.

The course of the isothermal decomposition of five compounds has been investigated nitrometrically at 40°. The data obtained are recorded graphically in Fig. 1. From these data the compounds may be listed in the approximate order of increasing stability as follows: $C_6H_5CO– < (C_6H_5)_2CH– < CH_3– < C_6H_5CH_2– < (C_6H_5)_3C–$. The benzyl and benzohydryl derivatives obviously undergo autocatalytic decomposition. The methyl- and phenyl-substituted methylazido-dithiocarbonates manifest a relative degree of stability reminiscent of the behavior of the substituted ammonium salts, of which the disubstituted derivative invariably differs from the mono-, tri- and tetra-substituted compounds in various physical properties, such as electrical conductivity.

Melting-point determinations were made with the aid of the Maquenne block,[6] an apparatus designed especially for use with substances which, like those under investigation, "melt with decomposition." Comparison

[6] Houben-Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, 1921, Vol. I, 2d ed., p. 734.

of the results obtained by this procedure with the melting points determined by the usual method, using a capillary tube (in an electrically heated Thiele apparatus), shows that the latter are usually lower in the case of compounds that undergo appreciable decomposition during fusion (see Table I).

Unlike the inorganic salts of the azido acid, the organic derivatives are not particularly explosive. They "puff" mildly when held in the flame, or when heated rapidly on a metal plate. Furthermore, on exposure to illumination they show no photosensitivity and undergo no coloration. This affords support to the photolytic theory mentioned in an earlier paragraph.

The results of qualitative determinations of the solubility of the compounds at room temperature in various non-aqueous solvents are presented in Table I. All of the organic derivatives studied were found to be insoluble in water and to be very soluble in chloroform.

TABLE I

MELTING POINTS AND SOLUBILITIES OF ORGANIC AZIDO-DITHIOCARBONATES

V = very soluble; M = moderately soluble; S = slightly soluble

R—SCSN$_3$ R =	Melting points, °C. Maquenne-block method	Melting points, °C. Capillary-tube method	Acetone	EtOAc	EtOH	MeOH	Ether	C_6H_6	CS_2	$CHCl_3$	CCl_4
CH_3—	32	34	V	V	M	M	M	V	V	V	V
$C_6H_5CH_2$—	64.5	66	V	V	S	S	M	M	V	V	M
$(C_6H_5)_2CH$—	67.5	67	V	V	M	M	M	V	V	V	V
$(C_6H_5)_3C$—	132 (dec.)	102–104 (dec.)	S	S	S	S	S	M	M	V	M
C_6H_5CO—	119–120 (dec.)	92–94 (dec.)	S	S	S	S	M	M	M	V	M
p-BrC_6H_4CO—	127 (dec.)	99–101 (dec.)	S	S	S	S	S	S	M	V	M

Analysis.—The amount of nitrogen evolved during thermal decomposition of the compounds was determined in each case by slowly heating the sample, mixed with sand to minimize the danger of explosion, in a bulb attached to a nitrometer. The results obtained were invariably somewhat high, as it was not feasible to introduce a correction for the vapor tension of the thiocyanate formed as a product of the reaction. The sulfur was determined as barium sulfate after conversion to a soluble sulfate by ignition with sodium peroxide in a Parr bomb.

Methyl Azido-dithiocarbonate, CH_3SCSN_3.—The product, which was obtained by the interaction of methyl bromide and sodium azido-dithiocarbonate in acetone, was purified by recrystallization from chloroform. It is slowly attacked by concentrated aqueous alkalies.

Anal. (a) Subs., 0.1855, 0.2498: $BaSO_4$, 0.6485, 0.8759. Calcd. for $C_2H_3N_3S_2$: S, 48.14. Found: S, 48.02, 48.16. (b) Subs., 0.4148, 0.2623: N_2 (corr.), 71.4, 44.7 cc. Calcd. for CH_3SCSN_3: N_2, 1 mole. Found: N_2, 1.023, 1.013.

Under the microscope the crystals appear to consist of thick, four-sided prisms which are rhomb-shaped in cross section. The acute angle of the rhomb is about 75°. The terminal pinacoid is perpendicular to the prism faces. All prism views exhibit parallel extinction; end views of the prisms reveal a very small extinction angle, about 1–2°. The angle of the acute bisectrix parallel to the elongation with 2V is about 65°. The crystals are optically negative and exhibit strong double refraction. They are probably of monoclinic symmetry.

Benzyl Azido-dithiocarbonate, $C_6H_5CH_2SCSN_3$.—The interaction of benzyl chloride and sodium azido-dithiocarbonate in acetone at room temperature required for its completion approximately twenty-four hours. The precipitated sodium chloride was filtered off and a small amount of water was added to the filtrate. The crude benzyl derivative which separated on cooling with ice and salt was purified by recrystallization from chloroform.

Most reagents cause primary decomposition of the azido-dithiocarbonate to form the thiocyanate, which then exhibits its own characteristic reactions. Thus, boiling with nitric acid brings about oxidation to benzaldehyde; the prolonged action of aqueous alcohol causes hydrolysis. Benzyl thiocyanate was obtained readily by heating the azido-dithiocarbonate in a suitable organic solvent (absolute alcohol) and removing the precipitated sulfur. The solution after concentration deposited crystals of benzyl thiocyanate, m. p. 41°.

Anal. (a) Subs., 0.1705, 0.1640: $BaSO_4$, 0.3768, 0.3675. Calcd. for $C_8H_7N_3S_2$: S, 30.64. Found: S, 30.35, 30.78. (b) Subs., 0.2021, 0.4856: N_2 (corr.), 21.62, 52.47 cc. Calcd. for $C_7H_7SCSN_3$: N_2, 1 mole. Found: N_2, 1.000, 1.010. (c) Dumas total nitrogen determination. Subs., 0.2611: N_2 (corr.), 42.5 cc. Calcd. for $C_8H_7N_3S_2$: N, 20.1. Found: N, 20.4.

Benzyl azido-dithiocarbonate crystallizes in prisms of monoclinic symmetry, showing the forms 1 0 0, 1 1 0, 0 1 1 and 1 0 1. Extinction is parallel to the plane of symmetry, and oblique in this plane at an angle of 7°: The crystals are biaxial, positive, 2V about 80°, $v < r$. The axial plane is transverse of the prisms. Double refraction is moderately strong.

Benzohydryl Azido-dithiocarbonate, $(C_6H_5)_2CHSCSN_3$.—The interaction of benzohydryl bromide[7] and sodium azido-dithiocarbonate in acetone was complete after about half an hour. After filtering to remove the precipitated sodium bromide, addition of water caused a yellow liquid to separate. This was dissolved in a mixture of petroleum ether and benzene and the solution was dried over anhydrous sodium sulfate. Upon cooling with ice and salt, benzohydryl azido-dithiocarbonate separated in small colorless crystals.

Anal. (a) Subs., 0.1113, 0.1340: $BaSO_4$, 0.1877, 0.2201. Calcd. for $C_{14}H_{11}N_3S_2$: S, 22.47. Found: S, 22.55, 22.56. (b) Subs., 0.4212, 0.5428: N_2 (corr.), 34.42, 42.68 cc. Calcd. for $C_{13}H_{11}SCSN_3$: Nz, 1 mole. Found: N_2, 1.017, 1.025.

The substance, recrystallized from xylene, forms prisms and elongated tablets, the opposite edges of which are beveled, and the ends obtusely pointed (120"). These tablets are frequently shortened to thick rhomb-shaped plates, the four vertices of which are beveled. Prism views exhibit parallel extinction; the rhombs, symmetrical extinction. End views show oblique extinction, about 45°.

Good biaxial interference figures are obtainable, which indicate that the acute bisectrix is inclined to the pinacoid of the tablets. The axial plane is parallel to the acute diagonal of the rhombs. Double refraction is strong, positive, with 2V about 60°,

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[7] The chloride reacted much more slowly, and for this reason was not as satisfactory as the bromide in this preparation.

and $r < v$ marked (or else inclined dispersion). Refractive indices were not determined on account of solubility in the standard immersion liquids. The oblique extinction of the end views of the prisms and tablets, and tilted position of the optic axes indicate that the plane symmetry of the crystals lies crosswise of them (parallel to the acute diagonal of the rhombs), and that they belong to the monoclinic system.

Triphenylmethyl Azido-dithiocarbonate, $(C_6H_5)_3C\text{-}SCSN_3$.—When triphenylmethyl chloride and sodium azido-dithiocarbonate were brought together in acetone, the ester was precipitated rapidly, together with sodium chloride. This precipitate was air-dried, and was extracted with chloroform, in which the triphenylmethyl ester is soluble. After concentrating and cooling, the solution deposited colorless crystals of triphenylmethyl azido-dithiocarbonate.

Anal. (a) Subs., 0.2743, 0.2348: $BaSO_4$, 0.3483, 0.3004. Calcd. for $C_{20}H_{15}N_3S_2$: S, 17.74. Found: S, 17.44, 17.57. (b) Subs., 0.3868, 0.3746: N_2 (corr.), 24.16, 23.37 cc. Calcd. for $C_{19}H_{15}SCSN_3$: N_2, 1 mole. Found: N_2, 1.008, 1.006.

The substance crystallizes in bipyramids and tablets of orthorhombic symmetry. The tablets possess end angles of about 120°. All views exhibit symmetrical extinction. The axial plane is parallel to the base of the pyramidal forms; 2V is large ($> 70°$). The crystals are optically positive.

Allyl Azido-dithiocarbonate, $C_3H_5SCSN_3$.—This substance was obtained by interaction of allyl bromide and sodium azido-dithiocarbonate in acetone. Because of the Instability and the difficulty of purification of the resulting product, no attempt was made to study it carefully. It apparently undergoes fairly rapid decomposition, since the characteristic odor of allyl isothiocyanate was very marked in all of the samples that were prepared.

Benzoyl Azido-dithiocarbonate, $C_6H_5COSCSN_3$.—This acyl derivative was prepared by the interaction of benzoyl chloride and sodium azido-dithiocarbonate, either in aqueous solution or in acetone. The latter medium is preferable, since the reaction is practically instantaneous in this solvent. The product was purified by recrystallization from chloroform.

Anal. (a) Subs., 0.1845, 0.2115: $BaSO_4$, 0.3810, 0.4348. Calcd. for $C_8H_5ON_3S_2$: S, 28.72. Found: S, 28.36, 28.24. (b) Subs., 0.2997, 0.2212: N_2 (corr.), 30.11, 22.33 cc. Calcd. for $C_7H_5OSCSN_3$: N_2, 1 mole. Found: N_2, 1.002, 1.006.

Benzoyl azido-dithiocarbonate is hydrolyzed by hot aqueous potassium hydroxide solution with the formation of potassium benzoate and potassium azido-dithiocarbonate. The formation of benzoyl isothiocyanate by the thermal decomposition of the benzoyl derivative is shown by the fact that the purified decomposition residue combines with alcohol to form ethyl benzoylthiocarbamate, $C_6H_5CO—NH—CS—OC_2H_5$, and with aniline to form α-phenyl-β-benzoylthiourea, $C_6H_5CO—NH—CS—NHC_6H_5$.[8] Apparently the strongly negative character of the benzoyl group causes the normal thiocyanate first formed to undergo immediately an intramolecular rearrangement to the isothiocyanate.

Benzoyl azido-dithiocarbonate crystallizes in the form of thin, oblique-ended plates, belonging to the monoclinic system; acute angles, 63°; obtuse angles, rarely truncated. When precipitated directly under the microscope, crystals are obtained in which the axial plane is inclined 21° to the longer edges of the plates, in the direction of the diagonal connecting their obtuse angles. Recrystallization from xylene alters the habitus so that the other two edges of the plates are longer, resulting in an apparent extinction angle of 6° instead of 21°. Seen edgewise the plates exhibit parallel extinction. They are optically negative, with 2V about 75–80°. The refractive index for vibrations in the

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[8] Miquel, *Ann. chim. phys.*, [5] 11, 321, 334 (1877).

axial plane is about 1.50; for vibrations transverse to this the refractive index is estimated to be about 1.75.

p-Bromobenzoyl Azido-dithiocarbonate, $BrC_6H_4COSCSN_3$.—This compound was precipitated, together with sodium chloride, by the interaction of p-bromobenzoyl chloride[9] and sodium azido-dithiocarbonate in acetone. The product was purified by recrystallization from chloroform.

p-Bromobenzoyl azido-dithiocarbonate crystallizes from chloroform or xylene in tiny rhomb-shaped plates or oblique-ended prisms. These exhibit oblique extinction. dispersed, at an angle of about 7–8°; some views show parallel extinction. It probably crystallizes in the monoclinic system.

Anal. (a) Subs., 0.2280, 0.1870: $BaSO_4$, 0.3503, 0.2857. Calcd. for $C_8H_4ON_3$-BrS_2: S, 21.22. Found: S, 21.10, 20.98. (b) Subs., 0.2580, 0.3497: N_2 (corr.), 19.44, 25.95 cc. Calcd. for C_7H_4OBr—$SCSN_3$: N_2, 1 mole. Found: N_2, 1.016, 1.001.

The reactions of the p-bromobenzoyl derivative are strictly analogous to those of the benzoyl compound. Boiling with aqueous potassium hydroxide solution hydrolyzes the substance to form potassium *p*-bromobenzoate and potassium azido-dithiocarbonate; thermal decomposition yields nitrogen, sulfur and p-bromobenzoyl isothiocyanate, which was identified by its melting point and by the preparation of its condensation product with alcohol and with aniline. Since p-bromobenzoyl isothiocyanate had not previously been prepared and described in the literature, it was necessary, for purposes of identification, to synthesize not only the isothiocyanate but also its condensation product with alcohol and with aniline. These are briefly described below.

_p_-Bromobenzoyl Isothiocyanate, BrC_6H_4CONCS.—This substance was readily obtained by the interaction of p-bromobenzoyl chloride and sodium thiocyanate in acetone. Recrystallization of the crude product from chloroform gave a colorless crystalline solid, m. p. 55°.

Anal. Subs., 0.2395, 0.2453: $BaSO_4$, 0.2242, 0.2323. Calcd. for C_8H_4ONBrS: S, 13.2. Found: S, 12.9, 13.0.

Ethyl **_p_-Bromobenzoylthiocarbamate,** BrC_6H_4CO-NH-CS-OC_2H_5.—This derivative was prepared by direct combination of ethyl alcohol with p-bromobenzoyl isothiocyanate. It crystallizes from aqueous alcohol in fine, colorless needles, m. p. 99°.

Anal. Subs., 0.2097, 0.2119: $BaSO_4$, 0.1675, 0.1690. Calcd. for $C_{10}H_{10}O_2NBrS$: S, 11.1. Found: S, 11.0, 11.0.

α-Phenyl-β-(_p_-bromobenzoyl)-thiourea, BrC_6H_4CO-NH-CS-NHC_6H_5.—This compound was produced by direct combination of aniline and p-bromobenzoyl isothiocyanate. Recrystallization from aqueous alcohol yielded a colorless crystalline solid, m. p. 151°. It is very soluble in chloroform, toluene and aniline; it crystallizes from the latter in the form of fine, elongated prisms.

Anal. Subs., 0.2648, 0.1810: $BaSO_4$, 0.1827, 0.1245. Calcd. for $C_{14}H_{11}ON_2BrS$: S, 9.6. Found: S, 9.5, 9.5.

Summary

The methyl, benzyl, benzohydryl, triphenylmethyl, benzoyl and p-bromobenzoyl azido-dithiocarbonates have been prepared and described.

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[9] p-Bromobenzoyl chloride may be prepared in good yield by the long continued action of an excess of thionyl chloride upon *p*-bromobenzoic acid, although the reaction is unusually slow. When 25 g. of thionyl chloride (0.21 mole) and 16 g. of the acid (0.08 mole) were refluxed for 120 hours, the yield of purified p-bromobenzoyl chloride, after one crystallization from petroleum ether, was 15 g. (85% of the calculated amount).

These compounds, the first organic derivatives of azido-dithiocarbonic acid to be isolated, were formed by interaction of the alkyl or acyl halide and sodium azido-dithiocarbonate in acetone. They are white, crystalline compounds, stable at 0°, but decomposing more or less rapidly at higher temperatures into thiocyanates or isothiocyanates, sulfur and nitrogen. The crystallographic properties, melting points and solubilities of the compounds have been determined. Unlike certain of the inorganic azido-dithiocarbonates, the organic compounds show no photosensitivity, presumably because of the molecular character of their lattices.

The preparation of *p*-bromobenzoyl isothiocyanate and its condensation products with alcohol and aniline is described.

ITHACA, NEW YORK

NOTES

The Rate of Rearrangement of Pinene to Dipentene.—The rate of disappearance of the optical activity of d-pinene upon heating has been measured by Smith.[1] His experimental results were treated by supposing that the reaction which occurred was a simple racemization, a view for which he presented some evidence. Recently it has been shown rather convincingly by Conant and Carlson[2] that the reaction Smith measured was the isomerization to dipentene. This substance is optically inactive and if the reaction went to completion the final rotation would be zero, just as in the supposed formation of the racemic mixture. The rate of the reaction, as calculated from the observed rotations, will not be the same in the two cases, and it is the purpose of this communication to point out how Smith's constants must be modified, if the reaction is actually an isomerization.

The equation appropriate to Smith's interpretation of the reaction was

$$\ln \alpha_1/\alpha_2 = 2k_1(t_2 - t_1) \qquad (1)$$

where α is a measured angle of rotation; but with the revised interpretation the rotation measures directly the amount of pinene remaining and we have

$$\ln \alpha_1/\alpha_2 = k_2(t_2 - t_1) \qquad (2)$$

This equation is of the same form as (1), and since Smith found that the values k_1 were constant, the values of k_2 will be constant also; clearly $k_2 = 2k_1$. That is, the correct first-order constants for the rearrangement are just twice the values reported by Smith.

It is still reasonable to suppose that this reaction occurs by a homogeneous unimolecular mechanism. Although it has lost some of its theoretical simplicity, since it can no longer be supposed that the heat of reaction is zero, it remains the only known example of a presumably unimolecular

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[1] Smith, THIS JOURNAL, **49,** 43 (1927)

[2] Conant and Carlson, *ibid.*, 51,3464 (1929).

rearrangement, since all the other first-order gas reactions are decompositions.

CONTRIBUTION NO. 256 FROM THE
GATES CHEMICAL LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA
LOUIS S. KASSEL[3]

RECEIVED NOVEMBER 25, 1929
PUBLISHED MAY 8, 1930

A Capillary Gas Valve.—Having had occasion to withdraw many small samples of extremely pure chlorine from a large storage bulb without contaminating the main supply, the scheme in Fig. 1 was adopted. The outer tube D is of thin-walled 12-mm. tubing, 30-cm. long; the capillary E is less than 1-mm. bore, with thin walls. When a sample is to be collected in the reaction vessel which, together with tube D, has been evacuated, liquid air is applied at G. From this point on, H serves as a chlorine block, cotton wrapping around H being continually soaked with liquid air throughout all subsequent operations. The Dewar flask is then removed, and the chlorine in capillary G begins to melt. Current sent through an electromagnet held at point A, Fig. 1, causes the iron-cored glass capsule C to jump up and break the capillary at point A, and chlorine in G begins to distil over into the reaction vessel. C is then pulled out of the way, as in Fig. 2. When sufficient chlorine has been collected, F is shut, and a small flame applied momentarily at B. Since the pressure in D is less than one atmosphere, the thin tube immediately collapses as represented by the dotted curve in Fig. 2. The flame is now directed at A, and the capillary quickly sealed off as shown in Fig. 3. The blob of glass may be pulled off subsequently to give the appearance of Fig. 1 again. The capillary always breaks at point A-B where the strain of being sealed to D lies. Any gases given off from the momentary heating at B can be pumped out of D before opening F to the reaction vessel again; and none of these gases can pass into the storage bulb against the stream of chlorine which continually evaporates from G and flows into D through

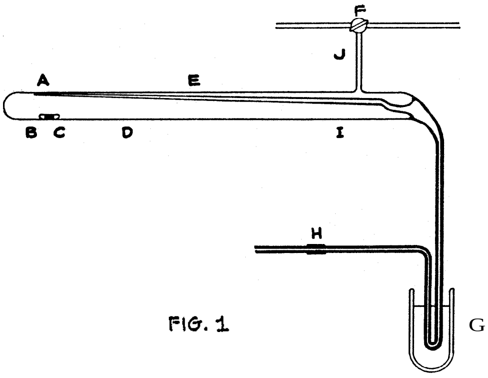

FIG. 1

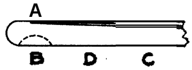

FIG. 2

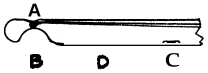

FIG. 3

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[3] National Research Fellow in Chemistry.

capillary E. The latter is sufficiently long to permit the withdrawal of about thirty samples, after which a new tube can be sealed on at I, and thirty more samples withdrawn. Stopcock F, treated with a special chlorine-resisting lubricant,[1] can be dispensed with, if necessary, by a slight modification of the scheme in Fig. 1, such as by sealing off the reaction vessel each time at a constriction at J.

This scheme is, of course, applicable to gases other than chlorine to replace other more complicated and less satisfactory devices. It has the advantage of repeated use without replacement. In other cases the liquid air trap may or may not have application, according to circumstances, and may be omitted at will.

CONTRIBUTION FROM THE
SCHOOL OF CHEMISTRY OF THE
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA
HUBERT N. ALYEA[2]
RECEIVED JANUARY 28, 1930
PUBLISHED MAY 8, 1930

A New Line in the Absorption Spectrum of Samarium.—During the course of work on the concentration of illinium it was noticed that an extremely faint line appeared at 5960 Å. in the absorption spectrum of supposedly pure samarium. No line at 5960 Å. has been reported for this element. As the material had been prepared by fractional crystallization of the double magnesium nitrates, the line could be attributed only to neodymium, europium, illinium or to samarium itself.

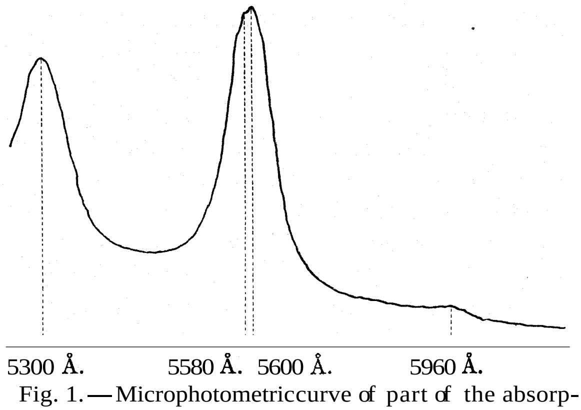

Fig. 1.—Microphotometric curve of part of the absorption spectrum of samarium nitrate, showing a new line at 5960 Å.

About two kilograms of rare earth oxide showing the line was, therefore, fractionally crystallized five hundred times as the double magnesium nitrate, and then one hundred times as the simple nitrate. During all this

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[1] H. N. Stephens, THIS JOURNAL, 52, 635 (1930).

[2] National Research Fellow.

time the line at 5960 Å. remained at the same relative intensity to the other lines of samarium throughout the series. The only impurity eliminated was a faint trace of neodymium, the absorption bands of which appeared quite distinct from the line in question. It was, therefore, concluded that the line at 5960 Å. belonged to samarium and had escaped observation before owing to its extreme faintness.

The figure shows a microphotometric curve taken from part of the absorption spectrum of samarium nitrate photographed on a Hilger E1 quartz spectrograph as described elsewhere.[1] The solution, which was 6.0 N in samarium nitrate, was in a 15-cm. absorption cell. The temperature was 80°, as the line is more intense when the solution is hot. Some idea of the relative intensities of the new line and the one at 5600 Å. may be gained from the figure.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

PIERCE W. SELWOOD

RECEIVED JANUARY 30, 1930
PUBLISHED MAY 8, 1930

The Standardization of Weights.—The accuracy of the Richards method[1] for the standardization of weights by substitution can be doubled by using the method of weighing by transposition. This latter method makes the use of a set of tare weights unnecessary, and involves no more time or difficulty than the Richards method. In fact, this is one operation to which the little-used transposition weighing seems peculiarly suited.

If the weights W_1 and W_2 are to be compared, W_1 is placed on the left pan and W_2 on the right and the zero point noted. The weights are then reversed and the difference, d, necessary to bring the pointer to the same zero point is noted. It can be shown readily that $W_2 - W_1 = d(l_2) \div (l_1 + l_2)$ where l_1 and l_2 are, respectively, the lengths of the beam to the left and to the right of the central knife edge. Since d is very small, any error introduced by assuming that $l_1 = l_2$ is entirely negligible, so $W_2 - W_1 = d/2$, where d may, of course, be either a positive or negative quantity. The method of calculating the corrections remains the same.

Variations in the relative lengths of the balance arms are not likely to occur during any one comparison, and variations between comparisons could not affect the value of $W_2 - W_1$ appreciably.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

PHILIP F. WEATHERILL

RECEIVED FEBRUARY 7, 1930
PUBLISHED MAY 8, 1830

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[1] Quill and Selwood with Hopkins, THIS JOURNAL, 50, 2929 (1928).

[1] T. W. Richards, *ibid.*, 22, 144 (1900).

[CONTRIBUTION PROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TENNESSEE]

A STUDY OF MOLECULAR ORGANIC COMPOUNDS. II. THE MOLECULAR ORGANIC COMPOUNDS OF 2,4-DINITROANILINE, 2,4-DINITROCHLOROBENZENE AND 2,4-DINITROBROMOBENZENE[1]

BY C. A. BUEHLER, ALAN HISEY AND JESSE H. WOOD

RECEIVED AUGUST 24, 1929 PUBLISHED MAY 8, 1930

This paper is a continuation of the study[2] of the molecular organic compounds of m-dinitrobenzene and some monosubstituted *m*-dinitrobenzenes. In the present investigation the effect upon molecular compound formation of introducing amino, chloro and bromo groups into m-dinitrobenzene has been determined. Quite a few compounds were isolated, some of their properties were determined, and the substitution compounds, into which some were easily converted, were identified.

Experimental Part

The molecular compounds were prepared for the most part as described previously. In a few cases it was not possible to purify by recrystallization due to decomposition. In two cases—the naphthols with 2,4-dinitrobromobenzene—carbon tetrachloride was found to be the best solvent for purification by crystallization. Substitution compounds were frequently obtained with the dinitrohalogenobenzenes. These were easily recognized by their color, solubility and melting points.

TABLE I

MOLECULAR COMPOUNDS OF 2,4-DINITROCHLOROBENZENE

Second component	M. p., °C. (corr.)	Color	Mol. ratio	From literature M. p., °C.	From literature Mol. ratio	Method of prepn.
a-Naphthylamine	72.0	Blood-red	1:1	69[a]	1:1	Soln.
				71.5	1:1[b]	F. p.
β-Naphthylamine	65.3	Garnet-red	1:1	65[a]	1:1	Soln.
Benzidine	68.8	Black	1:1[c]	......	..	...
Pyridine	189.6[d]	White	1:1	170–210[e]	1:1[e,1,2,3]	Soln.
Naphthalene	76.8	White	1:1	78[f]	1:1	Soln.
Fluorene	39[g]	Straw yellow	1:1	......	...	...
Diphenyl	31[g]	White	1:1	......	...	...
a-Naphthol	104.9	Deep yellow	1:1	......	...	..
@-Naphthol	91.2	Deep yellow	1:1	......	...	...

[a] Buguet, *Compt. rend.*, 151,312 (1910).

[b] Giua, Marcellino and Curti, *Gazz. chim. ital.*, 50, II, 300 (1920).

[c] It was not possible to obtain this compound in a quantity sufficient for an analysis. A few black crystals separated out with the bright red substitution compound, 2,4-dinitrophenylbenzidine. Since the latter is likely formed through the molecular com-

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[1] This paper is an abstract of the Master's Theses presented by Alan Hisey and Jesse H. Wood at the University of Tennessee.

[2] Buehler and Heap, THIS JOURNAL, 48,3168 (1926).

pound as an intermediate, it has been assumed that the former has a molecular ratio of 1:1.

[d] The melting point of this compound was not definite, due to decomposition.

[e] (1) The melting point of this compound was reported variously in the literature. Reitzenstein, *J. prakt. Chem.*, 68, II, 251 (1903), gave it as 201°; Gail in a Marburger Institute dissertation gave it as 210° according to Reitzenstein. (2) Zincke, *Ann.*, 333, 296 (1904), stated that the compound decomposed into its constituents at 200°. (3) Desvergnes, Mon. *sci.*, **15**, 73 (1925), reported *a* melting point of 170°.

[f] Willgerodt, *Ber.*, 11, 601 (1878).

[g] This melting point was an approximation. It could not be determined accurately by the ordinary method since the value is so near room temperature.

TABLE II

MOLECULAR COMPOUNDS OF 2,4-DINITROBROMOBENZENE

Second component	M. p., °C. (corr.)	Color	Mol. ratio	From literature M. p., °C.	From literature Mol. ratio	Method of prepn.
α-Naphthylamine	64.5	Blood-red	1:1	......	...	...
β-Naphthylamine	61.7	Blood-red	1:1	......	...	...
Pyridine	214[a]	Yellow	1:1	225 (dec.)[b]	1:1	Soln
Naphthalene	72.0	Straw yellow	1:1	......	...	...
or-Naphthol	97.9	Deep yellow	1:1	......	...	...
@-Naphthol	83.0	Orange yellow	1:1	......	...	...

[a] The melting point of this compound was not definite, due to decomposition.

[b] Zincke, *Ann.*, 333,296 (1904).

TABLE III

ANALYSES OF NEW MOLECULAR COMPOUNDS

( )-2.4-Dinitrochlorobenzene	Formula	Calcd.. %		Pound, %	
Fluorene-	$C_{13}H_{10}\cdot C_6H_3(NO_2)_2Cl$	Cl	9.63	9.55	9.43
Diphenyl-	$C_6H_5C_6H_5\cdot C_6H_3(NO_2)_2Cl$	Cl	9.95	9.64	9.53
or-Naphthol-	$C_{10}H_7OH\cdot C_6H_3(NO_2)_2Cl$	Cl	10.23	10.30	10.32
β-Naphthol-	$C_{10}H_7OH\cdot C_6H_3(NO_2)_2Cl$	Cl	10.23	10.30	10.35
( )-2,4-Dinitrobromobenzene					
α-Naphthylamine-	$C_{10}H_7NH_2\cdot C_6H_3(NO_2)_2Br$	Br	20.48	20.26	20.39
β-Naphthylamine-	$C_{10}H_7NH_2\cdot C_6H_3(NO_2)_2Br$	Br	20.48	20.21	20.16
Naphthalene-	$C_{10}H_8\cdot C_6H_3(NO_2)_2Br$	Br	21.31	21.26	21.40
or-Naphthol-	$C_{10}H_7OH\cdot C_6H_3(NO_2)_2Br$	Br	20.44	20.59	20.67
@-Naphthol-	$C_{10}H_7OH\cdot C_6H_3(NO_2)_2Br$	Br	20.44	20.56	20.41

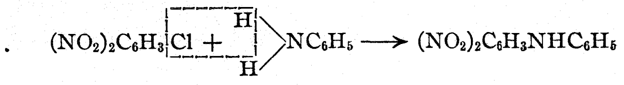
The analyses for halogens were carried out by Pringsheim's method.[3] The amount of silver halide was determined in some cases gravimetrically and in others volumetrically. The melting points were taken by Mulliken's[4] capillary tube method with a thermometer calibrated by the Bureau of Standards.

No molecular compounds of 2,4-dinitro-aniline were isolated.

[3] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1927, 4th ed., Vol. I, p. 147.

[4] Mulliken, "The Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 218.

Substitution Compounds of 2,4-Dinitrochloro- and 2,4-Dinitrobromobenzenes.—Second components containing amino groups did not readily form molecular compounds with the 2,4-dinitrohalogenobenzenes. Instead, substitution compounds were usually formed with the elimination of the hydrogen halide according to the scheme



$$(NO_2)_2C_6H_3Cl + \begin{matrix}H\\ \\H\end{matrix}\!\!>NC_6H_5 \longrightarrow (NO_2)_2C_6H_3NHC_6H_5$$

Aniline,[5] methylaniline,[6] diethylamine,[7] *p*-toluidine,[8,5] *o*-toluidine,[5] *p*-aminophenol,[9] *o*-,[10] *m*-[6] and *p*-phenylenediamines[11] reacted in this manner. Dimethylaniline reacted with the elimination of the methyl halide to form a substitution compound identical with that formed with methylaniline.[12] Benzidine[5,8] gave a few crystals of the molecular compound with the chloro compound, but substituted completely with the bromo compound. The a- and β-naphthylamines[13] formed fairly pure molecular compounds but these were readily converted into the corresponding substitution compounds by simply refluxing them for several hours in alcoholic solution. Of the two, the a-molecular compound was the more resistant to decomposition.

Discussion

Molecular Compounds are Intermediates in the Formation of Substitution Compounds.—The idea that reactions between organic compounds are due to an attraction between molecules resulting in an initial combination is not new.[14] Cases similar to those mentioned in this investigation are those of the addition compounds of picryl chloride with the a- and β-naphthylamines,[15] which readily lost hydrochloric acid to

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[5] Reitzenstein, Table I, Ref. el.

[6] Leyman, *Ber.*, 15, 1233 (1882).

[7] Romburgh, Rec. *trav. chim.*, **2**, 40 (1883).

[8] Willgerodt, Ber., 9, 977 (1876).

[9] Nietzki, ibid., 28, 2973 (1895).

[10] Borsche and Rantscheff, *Ann.*, 379, 169 (1911).

[11] Nietzki and Ernst, Ber., 23, 1852 (1890), gave the melting point of 2,4-dinitrophenyl-*p*-phenylenediamine as 177°; Morgan and Micklethwait, *J. Chem. Soc.*, 93, 610 (1908), stated that the compound melted at 190". Our result (177.8°) obtained repeatedly agreed more closely with the former. In addition the monoacetyl derivative, melting at 238°, checked the former's value.

[12] Leyman, Ref. 6, made this observation previously in the case of 2,4-dinitrochlorobenzene.

[13] Heim, *Ber.*, 21, 589, 2302 (1888).

[14] Kekulé, "Organische Chemie," Ferdinand Enke, Stuttgart, **1867**, Vol. II, p. 730; Guye, *J.* chim. *phys.*, 8, 119, 189 (1910); Schmidlin and Lang, Ber., 43, 2808 (1910); Giua, Marcellino and Curti, Table I, Ref. *b*.

[15] Sudborough and Picton, J. Chem. *Soc.*, 89, 583 (1906).

form the corresponding substitution products. Amines were particularly susceptible to molecular compound formation, but in most cases in this investigation substitution compounds were obtained. The α- and β-naphthylamines and benzidine were the sole amines which formed molecular compounds capable of being isolated. Since these were disrupted by moderate heat treatment in alcoholic solution, it seems reasonable to assume that molecular compounds were formed as intermediates in all cases of substitution.

Influence of the Substituent in a Dinitrobenzene on the Formation of Molecular Compounds.—Of the six dinitrobenzenes studied[16] each formed a different number of molecular compounds, a fact which shows that the substituent is an influencing factor. The groups arranged in the order of decreasing ability toward molecular compound formation are: $Cl > Br^{17} > OH > H > CH_3 > NH_2$. This order is the same as the electronegative character of these groups.[18]

Kendall[19] stated, from the results of a series of experiments, that addition compounds will be formed between two components if there is sufficient difference in acidic strength. Increasing the electronegative character of any substituent in a benzene ring should increase the acidic strength of the compound and, therefore, increase the number of possible molecular compounds. The results of this investigation with the amine molecular compounds bear out this relation. In the case of the hydrocarbon and phenol molecular compounds the number obtained was so small that no conclusions can be drawn in regard to this relation.

The Structure of Molecular Organic Compounds.—The electronic conception of valency as introduced by Lewis[20] has been very helpful in that it does account for the differences between inorganic (polar) and organic (non-polar) compounds. Quite recently Sidgwick[21] has applied it to the Werner complexes, solvation and various other chemical phenomena. His success in this work has raised the question: Can molecular compound formation be explained using the electronic interpretation of valency?

Bennett and Willis[22] have proposed formulas for the compounds formed between nitro compounds and amines and hydrocarbons. These investigators assumed that the union takes place by means of co-valent linkages

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[16] Three were reported previously, Buehler and Heap. Ref. 2.

[17] Chlorine and bromine have been placed before the hydroxyl group since it has been assumed that the great number of substitution compounds of the former two implies the previous existence of molecular compounds.

[18] Crocker, *ibid.*, 44, 1618 (1922).

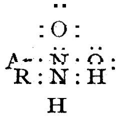
[19] Kendall, *ibid.*, *36*, 1722 (1914).

[20] Lewis, This Journal, 38,762 (1916).

[21] Sidgwick, "The Electronic Theory of Valency," Oxford University Press.

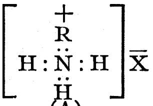
[22] Bennett and Willis, J. *Chem. Soc.*, 256 (1929).

and that the nitro group is the point of attachment[23] in the nitro compound. Their representation of an amine nitro compound would be as indicated. Here the amine is the donor and the nitro compound the acceptor.

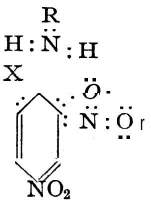

$$\begin{array}{ccccc} & & \overset{..}{:O:} & & \\ A\leftarrow & : & \ddot{N} & : & \ddot{O}: \\ R & : & N & : & H \\ & & H & & \end{array}$$

There is considerable evidence supporting this coordinate co-valent type of union in molecular compounds. In the first place mention may be made of the low melting points[24] of these compounds—all of them melted lower than the higher-melting component with the exception of the *α*-naphthol molecular compound. Again, the fact that the great majority of these consist of two molecules in a one-to-one ratio can best be explained upon the basis of a union of a co-valent type between atoms. The color which some of these show may also be interpreted in terms of this type of combination.[22]

Assuming a coordinate co-valent type of union, how can the molecular compounds formed in this investigation be best represented? In the case of the amine molecular compounds, the amine is undoubtedly the donor compound. It reacts with acids to form compounds of the type shown (A).[25] In this investigation the dinitrobenzenes were the acids and as such they may be considered as reacting to form ortho or para quinoid inner salts corresponding to the salts which trinitrobenzene forms with potassium methylate.[26]


$$\left[\begin{array}{c} + \\ R \\ H:\ddot{N}:H \\ \ddot{H} \end{array}\right]\bar{X}$$
(A)

The highly colored compounds resulting from their union with amines may then be represented as shown in diagram (B),[27] where X = Cl, Br, OH,[28] H or CH_3. In cases where X = Cl or Br, this complex was not stable with the more basic amines due to the fact that the halogen was eliminated with one of the hydrogens of the amino group, with the result that the arylimido group occupied the position (1) alone. With pyridine (when X = Cl) this complex seemed to have only a temporary existence.[29] Here, there were no hydrogen atoms attached to the nitrogen atom of the pyridine ring. For that reason the halogen was not eliminated as the halogen hydride but it ionized, resulting in the formation by rearrangement of the complex salt (C). This repre-



(B)

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[23] Brewin and Turner, J. Chem. *Soc.*, 334 (1928).

[24] Sidgwick, "The Electronic Theory of Valency," p. 105.

[25] Lewis, "Valency and the Structure of Atoms and Molecules," p. 87.

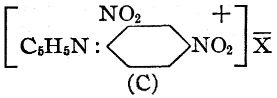
[26] Meisenheimer, ***Ann.***, 323,205 (1902).

[27] Sudborough and Beard, **J. *Chem. Soc.***, 97,773 (1910).

[28] The lack of color in some of the amine-2,4-dinitrophenol compounds seems to indicate that the attachment occurs between the lone pair of the amine and the hydrogen atom of the phenolic group. Additional support to this structure is furnished by the numerous amine–phenol compounds that are known.

[29] The compound, at first violet, showed signs of melting below 100"; the red droplets which appeared soon disappeared and the compound turned white and melted as reported above.

sentation explains very well the properties of the pyridine compounds with 2,4-dinitrochloro- and 2,4-dinitrobromobenzenes.



(C)

They are white or almost so, are soluble in water, have a high melting point and in aqueous solution they precipitate their halide atoms quantitatively with silver nitrate. In other words they are salts and therefore polar compounds.

The authors are greatly indebted to the Department of Chemistry, The Ohio State University, for the use of their library facilities.

Summary

1. New molecular organic compounds of 2,4-dinitrochlorobenzene and 2,4-dinitrobromobenzene have been isolated; no similar compounds with 2,4-dinitro-aniline could be isolated.

2. It has been shown in some cases that substitution products resulted through the intermediate formation of molecular compounds.

3. The influence of the substituent in the dinitrobenzenes upon molecular compound formation is discussed.

4. An electronic formula is proposed for the amine molecular compounds.

KNOXVILLE, TENNESSEE

[THE RESULTS PRESENTED IN THIS PAPER WERE OBTAINED PRIVATELY IN THE ORGANIC LABORATORY, BUREAU OF SCIENCE, MANILA, PHILIPPINE ISLANDS]

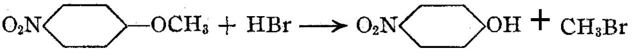
PHENOLIC DECOMPOSITION' OF CERTAIN MIXED ETHERS. THE VELOCITY CONSTANT

BY D. M. BIROSEL[1]

RECEIVED NOVEMBER 19, 1929 PUBLISHED MAY 8, 1930

Introduction

It is well known that mixed ethers, *e.* g., *p*-nitrophenyl methyl ether will give the corresponding phenol as one of the products of reaction according to the scheme



when they are acted upon by hydrogen bromide. Graebe and Martz[2] and also Raiford and Colbert[3] digested certain mixed ethers with 48% hydrobromic acid alone on the steam-bath for two hours and obtained varying degrees of decomposition depending upon the kind and number of substituents actually present in the phenyl residue. Stoermer[4] carried out

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[1] Formerly Research Chemist of the Laboratory Products Company, Cleveland, Ohio.

[2] Graebe and Martz, Ann., 340,220 (1905).

[3] Raiford and Colbert, THIS JOURNAL, 48, 1776 (1926).

[4] Stoermer, Ber., 41, 321 (1908).

the decomposition with acetic acid as reaction medium and reported varying extents of decomposition depending upon whether the substituent occupied the ortho or para position in the benzene nucleus. The kinetics of this reaction does not seem to have been investigated and it seemed interesting to study the factors influencing the phenolic decomposition of mixed ethers.

Experimental Part

A. Preparation of Materials

2,4-Dibromophenyl Methyl Ether.—Twenty grams of unsubstituted anisole dissolved in 20 cc. of chloroform was treated according to the procedure of Raiford and Birosel,[5] with 59.14 g. of bromine dissolved in 20 cc. of the same solvent. The mixture was allowed to stand at room temperature for four days, after which it was freed from the unused bromine by washing with a dilute solution of sodium hydroxide, then with distilled water, and dehydrated with anhydrous sodium sulfate. The solvent was evaporated and the residue consisted of solid and liquid derivatives. The solid was separated and crystallized from alcohol, giving shiny scale crystals melting sharply at 63°.[6]

***p*-Bromophenyl** Methyl Ether.—The liquid obtained above was found to distil mostly at 223°. It was redistilled and the portion going over at 223°[7] was reserved.

o-Bromophenyl Methyl Ether.—Ten grams of unsubstituted anisole was treated as above with the required amount of bromine for a monomolecular proportion. A liquid was obtained which distilled at 210–213°. It was redistilled and the fraction going over at 210°[8] was reserved for use.

2,4,6-Tribromophenyl Methyl Ether.—This compound was prepared as above by treating 10 g. of 2,4-dibromophenyl methyl ether with the required amount of bromine for a monomolecular proportion. After four days the solvent and unused bromine were removed. Two distinct crystal forms were obtained when the residue was crystallized from alcohol. The needle crystal material was separated from the shiny scale crystals of dibromo-anisole and recrystallized from alcohol, giving a product which melted sharply at 87°.[9]

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[5] Raiford and Birosel, This Journal, 51, 1652 (1929).

[6] Cahours, Ann., 52,331 (1884), obtained a liquid monobromo derivative of which he did not mention any characteristic and 2,4-dibromo-anisole, which gave shiny scale crystals, m. p. 54°, from alcohol, when he brominated anisole. Korner, *ibid.*, 137, 206 (1866), prepared 2,4-dibromophenyl methyl ether from 2,4-dibromophenol, sodium methoxide and methyl iodide and obtained shiny scale crystals, m. p. 59°. Kohn and Pfeifer, Monatsh., 48, 211 (1927), prepared 2,4-dibromophenyl methyl ether from 2,4-dibromophenol obtained by the reduction of *sym.*-tribromophenol, with potassium hydroxide and dimethyl sulfate. Crystallizing from alcohol they obtained shiny scale crystals which they reported as melting from 62 to 64°.

[7] Henry, *Ber.*, 2,711 (1869), prepared p-homo-anisole by treating anisole with one molecular proportion of phosphorus pentabromide. He obtained a liquid which distilled at 220° (uncorrected). Autenrieth and Mullinghaus, *Ber.*, 39, 4098 (1906), prepared this compound in the same way as Henry and obtained a liquid boiling between 213 and 216°.

[8] Michaelis and Geisler, *ibid.*, 27, 256 (1894), prepared o-bromo-anisole according to the directions of Mulhauser, Ann., 207,239 (1881), from *o*-anisidine, $CH_3OC_6H_4NH_2$. They obtained a liquid boiling at 210°.

[9] Kohn and Fink, Monatsh., 44, 18 (1923), prepared *sym.*-tribromo-anisole from 2,4,6-tribromophenol (1 mole), potassium hydroxide (10% solution) and dimethyl sulfate

B. Procedure of Decomposition

The velocity and extent of the phenolic decomposition of mixed ethers were determined at the temperature of the steam-bath. A weighed amount of the ether was digested with 30 cc. of constant boiling hydrobromic acid in glacial acetic acid solution made by adding 150 cc. of 48% hydrobromic acid to 300 cc. of acetic acid, for the desired period of time. The mixture was cooled and sodium hydroxide solution (1:4) was gradually added until the solution became slightly alkaline. The undecomposed ether was recovered by three ether extractions, washing each extraction with distilled water and adding the washings to the alkaline solution. Dilute sulfuric acid was added to the alkaline solution until slightly acidic and the phenol was extracted three times with ether. The solvent was evaporated, the residue heated on the steam-bath until the odor of acetic acid was no longer noticeable and then dehydrated in a desiccator.

The results obtained from experiments are given in the tables.

TABLE I

EXTENT OF DECOMPOSITION OF CERTAIN MIXED ETHERS

Compound	Time, hours	Ether used, g.	HBr used, cc.	AcH used, cc.	Acid soln. used, cc.	Phenol obtained, g.	Decomposition, %
o-Bromo-anisole	2	1.6835	10'	20	30	0.4135	26.57[a]
	4	1.0840	10	15	25	.8755	87.28
p-Bromo-anisole	2	2.1500	15	25	40	1.5437	77.60[a]
2,4-Dibromo-anisole	2	1.0000	10	10	20	0.2035	21.48
	2	1.0000	10	20	30	.1710	18.05
2,4,6-Tribromo-anisole	2	0.5000	10	20	30	.1885	39.40

[a] Stoermer, Ref. 4, obtained 67.8% decomposition of o-bromo-anisole for four hours of digestion and 75% decomposition of *p*-bromo-anisole for two hours of digestion. He did not give data from which his figures can be recalculated.

TABLE II

THE RATE OF DECOMPOSITION OF 2,4-DIBROMOPHENYL METHYL ETHER IN GLACIAL ACETIC ACID AS MENSTRUM

Expt.	Time, minutes	Ether used, *g.*	Acid soln. used, cc.	Dibromophenol obtained, *g.*	Calcd. decomposed ether, *g.*	Decomposition, %	k
1	60	1	30	0.0965	0.1025	10.19	0.00180
2	90	1	30	.1375	.1458	14.79	.00178
3	120	1	30	.1705	.1807	17.19	.00166
4	150	1	30	.2508	.2658	18.05	.00206
5	240	1	30	.3270	.3466	34.51	.00177
6	360	1	30	.4460	.4728	46.55	.00178
7	480	1	30	.5080	.5385	55.04	.00161
8	600	1	30	.5650	.5989	59.64	.00152

($1^1/_4$ mole). Crystallizing from alcohol, they obtained needle crystals melting at 87°. Reinecke, *Z. Chem.*, 366 (1866), reported that by using three molecular proportions of bromine on anisic acid (*p*-carboxyanisole), 2,4,6-tribromophenyl methyl ether melting at 87° was obtained.

Table III

The Rate of Decomposition of 2,4-Dibromophenyl Methyl Ether as Influenced by Varying the Amount of Halogen Acid in Glacial Acetic Acid as Menstrum

Expt.	Time, minutes	Ether used, g.	HBr used, cc.	AcH used, cc.	Acid soln. used cc.	Dibromo-phenol[a] obtained, g.	Calcd. decomposed ether, g.	Decompo-sition, %	k
1	60	1	10	10	20	0.2035	0.2157	21.48	0.00202
2	60	1	10	20	30	.1705	.1807	17.19	.00166
3	60	1	10	30	40	.1130	.1198	12.04	.00106
4	60	1	10	40	50	.0880	.0933	0.27	.00082
5	60	1	20	10	30	.2179	.2310	23.00	.00219
6	60	1	30	10	40	.2250	.2385	23.75	.00227
7	60	1	40	10	50	.2300	2438	24.28	.00233

[a] A nitro derivative, 2,4-dibromo-6-nitrophenol was prepared according to the directions of Kohn and Pfeifer, Ref. 6; crystallization from alcohol gave small yellow plate crystals melting at 118°.

Table IV

The Rate of Decomposition of 2,4-Dibromophenyl Methyl Ether in Formic Acid as Menstrum

Expt.	Time, minutes	Ether used, g.	Acid soln. used, cc.	Dibromo-phenol obtained, g.	Calcd. decomposed ether, g.	Decomposi-tion, %	k
1	120	1	30	0.0140	0.0148	1.48	0.00012
2	180	1	30	.0220	.0233	2.32	.00013
3	240	1	30	.0240	.0254	2.53	.00011

Table V

The Rate of Decomposition of 2,4,6-Tribromophenyl Methyl Ether in Glacial Acetic Acid as Menstrum

Expt.	Time, minutes	Ether used, g.	Acid soln. used. cc.	Tribromo-phenol[a] obtained, g.	Calcd. decomposed ether, g.	Decomposi-tion, %	k
1	60	0.5000	30	0.1085	0.1128	22.68	0.00426
2	120	.5000	30	.1885	.1960	39.60	.00415
3	240	.5000	30	.3005	.3125	62.83	.00409
4	360	.5000	30	.3780	.3931	79.04	.00392
5	360	.3700	15	.2602	.2720	79.59	.00369

[a] Crystallization from alcohol gave fine needle crystals, m. p. 92°; the melting point recorded in the literature for *sym.*-tribromophenol is 92–95°.

C. Discussion

In Table I are given the detailed results of the extent of decomposition of four bromo derivatives of anisole. Comparison of the decomposition for an interval of two hours shows that 2,4-dibromophenyl methyl ether is the least decomposed, that 2,4,6-tribromophenyl methyl ether appears to give higher phenolic decomposition than the dibromo derivative, and that o-bromo-anisole is more resistant to phenolic decomposition than the *p*-bromo derivative.

In Table II are shown the results of a typical experiment on the velocity of the phenolic decomposition of mixed ethers at the temperature of the steam-bath. The rate constants, k, are those calculated from the integrated form of the differential equation for first-order reactions, using logarithms to the base e. It will be noted that the constancy of k is quite satisfactory. The calculated amount of decomposed ether was obtained by multiplying the amount of dibromophenol obtained directly from experiment by the factor 1.06.

Table III shows the effect of changing the amount of hydrobromic acid in glacial acetic acid solution upon the phenolic decomposition of 2,4-dibromophenyl methyl ether. The greater the amount of halogen acid used, the greater the degree of decomposition and the higher the rate constant becomes. This does not mean that decomposition is greater when the halogen acid is used alone. Digesting a weighed amount of the ether for several hours on the steam-bath with hydrobromic acid alone did not give appreciable decomposition, which experience led to the employment of glacial acetic acid as menstrum. The solvent, though not entering into the reaction, seems to play an important role. In Table IV are expressed the results obtained from experiments when formic acid was used in place of glacial acetic acid. The extent of decomposition and the rate constant calculated in the same manner as the velocity constant in Table III are very much lower.

In Table V are given the detailed results of the experiments on the decomposition of 2,4,6-tribromophenyl methyl ether. The rate constants are those calculated from the integrated forms of the differential equation for first-order reactions, using logarithms to the base e. It will be noted that the constancy of k is quite satisfactory. The calculated amount of decomposed ether was obtained by multiplying the amount of tribromophenol obtained directly from experiments by the factor 1.04.

Summary

1. The kinetics of the phenolic decomposition of mixed ethers has been studied in the case of 2,4-dibromophenyl methyl ether and with 2,4,6-tribromophenyl methyl ether. Experiments were made in glacial acetic acid and formic acid as menstrums.

2. The velocity constants of the decomposition of 2,4-dibromophenyl methyl ether and 2,4,6-tribromophenyl methyl ether were calculated from the experimental results and their constancy is quite satisfactory. The phenolic decomposition of mixed ethers appears to be a first-order reaction.

3. The extent of decomposition is proportional to the amount of halogen acid used and seems to be influenced by the reaction medium. Decomposition is greater in glacial acetic acid than in formic acid as menstrum.

4. The degree of decomposition is also influenced by the number of substituents actually present and the position occupied in the phenyl residue.

The kinetics of the decomposition of other mixed ethers is being studied.

PASAY, RIZAL, PHILIPPINE ISLANDS

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 240]

QUALITATIVE ESTIMATION OF THE COMPOSITION OF BUTENE MIXTURES BY DISTILLATION METHODS[1]

BY HOWARD J. LUCAS,[2] ROBERT T. DILLON[3] AND WILLIAM G. YOUNG[3]

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Introduction

This paper describes some of the preliminary work done in studying methods for the analysis of the normal butenes, as follows: separation of dibromobutanes by fractional distillation at 50 mm.; separation of butenes by fractional distillation at atmospheric pressure; the reaction of 1-butene with hydrogen bromide.

Preparation of Dibromobutanes

Materials.—Eastman's 1-butanol No. 50, b. p. 116–118°, was slowly distilled through a 75 × 3 cm. fractionating column of cut-glass rings. The reflux ratio was ten to one. The fraction between 117.2 and 117.4° at 746.6 mm., which constituted about 85% of the whole, was collected. The 2-butanol[4] was similarly distilled and the fraction distilling at 98.8–99.0° at 745.3 mm was used. This had a refractive index n_4^{20} 1.3976, in satisfactory agreement with 1.397.[5] Merck's bromine was shaken with a solution of potassium bromide and distilled from concentrated sulfuric acid.

The aluminum oxide catalyst was prepared by precipitating aluminum hydroxide from a 5% solution of aluminum nitrate by the addition of dilute ammonium hydroxide. The precipitate was filtered off with suction, the solid was thoroughly agitated with a volume of water half that of the original solution and filtered again. The process was repeated. The final product was dried at 110–115° and broken into small pieces, the maximum dimensions being about 5 mm. This material was placed in the reaction tube and heated to 320–360° for four hours while air was drawn through. Some water was given off. The catalyst was now ready for use.

Decomposition of the Alcohols.—The alcohols were decomposed in the apparatus shown in Fig. 1. The alcohol, as it dropped from the graduated container into the heated tube, was volatilized and passed into a pyrex tube, 2.5 X 80 cm. The first half served as a preheater and the second half contained the aluminum oxide catalyst packed for a length of 25 cm. As the gas entered the reaction zone from the preheater the temperature was 205° for the 1-butanol and 250° for the 2-butanol, while the catalyst was maintained at 330–340° for the first, and 310–320° for the second alcohol. The average rates

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[1] This paper contains results obtained in an investigation listed as Project No. 14 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Committee of the National Research Council.

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[3] American Petroleum Institute Research Assistant.

[4] We have been aided in this research by the Stanco Distributors, Inc., New York, who through the courtesy of Mr. C. L. Bowman have kindly supplied us with pure 2-butanol.

[5] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1926, Vol. I.

of flow were 35 g. and 25 g. per hour, respectively. The butene was cooled first in the condenser, then in the ice trap in order to condense water and unchanged alcohol, and then, after bubbling through 23% perchloric acid and drying with calcium chloride, passed into the all-glass reaction flask maintained at −15 to −20° and so arranged that it could be easily shaken. Except at the beginning and at the very end of the experiment butene was always in excess, the bromine being added slowly and at intervals. The possibility of substitution taking place with the production of tribromobutanes and monobromobutane was small. The resulting dibromobutane was shaken once each with cold water and dilute sodium sulfite solution, then twice with water and dried over calcium chloride. The yield was 85% on the alcohol reacted (corrected for that recovered) and 99% on the bromine.

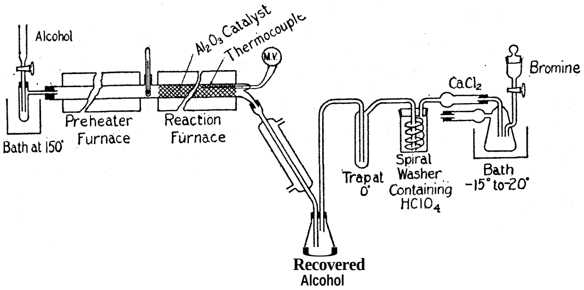

Fig. 1.—Apparatus used in the decomposition of the butanols over aluminum oxide.

Fractional Distillation of the **Dibromobutanes.**—The dibromobutane mixtures were fractionally distilled at 50-mm. pressure in the apparatus shown in Fig. 2. The material was placed in the flask B and when heated by the electric heater A boiled in a satisfactory manner without much bumping. (Pieces of scrap platinum or of anhydrous calcium chloride were found to be an aid.) The flask was attached by means of a ground-glass joint to the fractionating tube, 2 × 95 cm., containing a 70-cm. column of cut-glass rings and provided with a reflux condenser at the top. In lieu of a vacuum jacket, the tube was surrounded for a length of 70 cm. with a 5-cm. layer of mineral wool[6] packed in

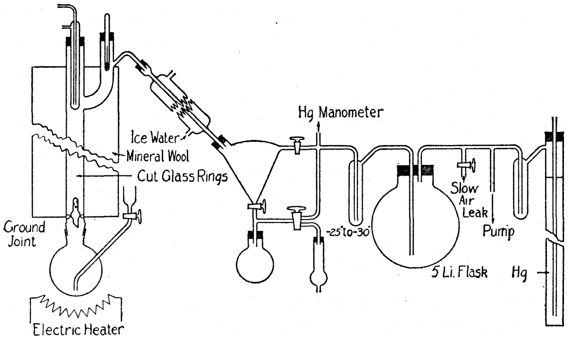

Fig. 2.—Apparatus used for fractionally distilling dibromobutanes at 50 mm. pressure.

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[6] Supplied by the Mineral Wool Products Co., Torrance, Calif. This material has a lower heat conductivity than 85% magnesia, ground cork or pure wool, and gave satisfactory insulation.

a stove pipe. The cuts were made in the usual manner and the fractions were introduced into the distilling flask at the proper time through the side arm. The pressure was maintained at 50 mm. by a regulating device similar to that used by Schofield,[7] except that the greater part of the entering air came through a slowly leaking stopcock instead of through the mercury regulator. This gave a more uniform pressure. Fifty mm. was selected as the working pressure in order to have a satisfactory distilling temperature and one where decomposition and isomeric change would be negligible, since in the distillation at atmospheric pressure, hydrogen bromide is often evolved while on heating to higher temperatures isomeric change has been noted.[8]

Of the dibromides, 400 g. from 1-butanol and 480 g. from 2-butanol were systematically fractionated by six distillations. A comparison of the properties of the fractions with those of the pure dibromides, which were distilled in the same apparatus, and a consideration of the distribution of material in the various fractions shows that the separation was not complete. The densities, d_4^{20}, of the 80.5–81.0° fraction in the first experiment and of the 79.0–80.2° fraction in the second were both 1.7938, whereas that of pure 1,2-dibromobutane, b. p. 80.5–80.7° at 50.0 mm., is 1.7951. The incompleteness of the separation was also proved by the analysis of the largest (5th) fraction in the second experiment by the method subsequently developed,[9] which instead of pure higher boiling 2,3-dibromobutane showed 2.0% of 1,2-dibromobutane, 74.7% of higher boiling and 23.2% of lower boiling 2,3-dibromobutane. The separation, however, appears to be as good as or better than that obtained by Lépingle after ten distillations of a similar product.[10] These materials were used for preliminary work on reaction rates.

Butene from 2-Bromobutane

Preparation.—Butene was obtained in 85% yield from the action of 400 g. of potassium hydroxide in 600 g. of 95% ethanol upon 305 g. (2.23 moles) of 2-bromobutane, b. p., 89.8–89.9°, prepared from 2-butanol and 48% hydrobromic acid. The butene was generated in a suitable flask heated in an oil-bath at 128°, washed with 30% methanol and pure water in two scrubbing towers, passed through one tower of soda lime and three towers of anhydrous calcium chloride and collected in tubes immersed in ice–hydrochloric acid mixture. The tubes were sealed off.

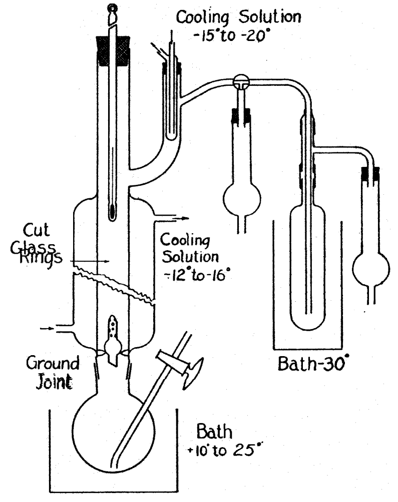

Fig. 3.—Apparatus used for fractionally distilling butenes at atmospheric pressure.

Distillation of the Butene Mixture.—The mixed butenes resulting from the decomposition were fractionally distilled through a 60-cm. column of cut-glass rings kept cold by the circulation of ice-hydrochloric mixture at –10 to –15° through an outer jacket and provided at the top with a reflux condenser cooled with brine at –14 to –18° for the purpose of insuring a rapid run-back of liquid, Fig. 3. This is the same

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[7] Schofield, Ind. Eng. *Chem.*, 18,717 (1926).

[8] Favorsky, *Ann.*, 354,370 (1907).

[9] Dillon, Young and Lucas, THIS JOURNAL, 52,1953 (1930).

[10] Lépingle, Bull. *soc. chim.*, 39,741 (1926).

apparatus as that used in the final distillation of the isomeric 2-butenes.[11] Cuts were made at intervals of 0.5 and 1.0°, the latter where the temperature increased the more rapidly, for example between -5.5 and $+0.5°$. The butene was sealed off in the tubes in which it was collected and when needed was transferred to the distilling flask through the side arm, usually without material loss. Occasionally a part or all of the butene was lost. After four distillations the 1-butene, b. p. -6.7 to $-6.5°$, was fairly well separated, and apparently constituted 15 to 20% of the total. However, there was very little separation of the isomeric 2-butenes, b. p. 0.3 and 3.0°, respectively, the temperature rising gradually from 0 to 2°. The separation of any considerable quantity of a pure 2-butene from its stereoisomer by fractional distillation would appear to be impractical. Coffin and Maass[12] collected a fraction of 2-butene, free from 1-butene, over the temperature range of 1.5–1.7° for their physical measurement work. It is evident that their product was a mixture of the stereoisomeric forms.

Hydrogen Bromide and 1-Butene

Materials.—The 1-butene was synthesized from allyl bromide and methyl magnesium iodide,[13] the fraction used distilling at -6.6 to $-6.4°$ in the apparatus described above (yield was 68%). The 1-bromobutane and 2-bromobutane, on which densities and refractive indices were taken, were prepared in amounts of 215 g. and 180 g. by the action of 48% hydrobromic acid upon pure specimens of the respective alcohols. After careful washing and drying, the bromides on distillation gave fractions of i7C g. and 160 g., respectively, at constant temperatures of 101.5 and 89.8°.

Procedure.—22.4 g. (0.40 mole) of 1-butene was distilled into a solution of 41.0 g. (0.51 mole) of hydrogen bromide in 50 g. of glacial acetic acid at -18 to $-20°$. The tube containing the mixture was sealed off and left in the ice box at 5° for three days. The tube was opened, the contents poured into ice water, the bromide layer separated and washed in succession with dilute sodium bisulfite, water, cold concentrated sulfuric acid, water, dilute sodium bicarbonate and water. The yield was 63%. The product, after drying over anhydrous potassium carbonate, was distilled, 80% coming over at 90.0–90.2' and 95% up to 90.4'. By taking refractive indices on different fractions it was shown that the 3% fraction, 90.4–91.0°, was practically identical with the rest. A comparison of the refractive indices and densities of pure 1-bromobutane, pure 2-bromobutane and of the reaction product, Table I, shows the latter to be 2-bromobutane containing not more than 3% of 1-bromobutane. The reaction of 1-butene with hydrogen bromide is therefore of no use as a means of analyzing a mixture of 1- and 2-butene since they both yield the same product.

TABLE I

PHYSICAL PROPERTIES OF BROMOBUTANES

	B. p., °C. (corr.)	Pressure mm.	Density in *vacuo* d_4^{20}	d_4^{25}	Refractive index n_D^{20}
1-Bromobutane	101.5	744	1.2756	1.2686	1.4403
2-Bromobutane	89.8	744	1.2607	1.2534	1.4374
Reaction product	90.0–90.2	...	1.2609	.....	1.4374

The densities were taken in a 10-ml. pycnometer and are corrected to vacuum.'' The refractive indices were taken with an Abbé refractometer, standardized at the time.

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[11] Young, Dillon and Lucas, THIS JOURNAL, 51,2528 (1929).

[12] Coffin and Maass, *ibid.*, 50, 1427 (1928).

[13] Lucas and Dillon, *ibid.*, 50, 1460 (1928).

[14] Reilly, Rae and Wheeler, "Physico-Chemical Methods," D. Van Nostrand Co., New York, 1925, p. 322.

Summary

The dehydration of 1-butanol and 2-butanol over aluminum oxide at 300–350° gave butenes which were converted to the bromides. By means of fractional distillation at 50 mm. the three component dibromobutanes were separated from one another but not in a pure state. The approximate compositions of the butene mixtures were 68% 1-butene, 12% 2-butene, b. p. 0.3' and 20% 2-butene, b. p. 3.0° from 1-butanol and 26, 26 and 48%, respectively, from 2-butanol.

The butene mixture obtained from 2-bromobutane was partially separated by fractional distillation. It contained 15–20% of 1-butene, the balance consisting of a mixture of the isomeric 2-butenes.

When hydrogen bromide in glacial acetic acid reacted with 1-butene, the product was practically pure 2-bromobutane.

PASADENA, CALIBORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 241]

THE REACTION RATES OF POTASSIUM IODIDE WITH 1,2- AND 2,3-DIBROMOBUTANE. THE ANALYSIS OF MIXTURES OF THE NORMAL BUTENES[1]

BY ROBERT T. DILLON,[2] WILLIAM G. YOUNG[2] AND HOWARD J. LUCAS[3]

RECEIVED NOVEMBER 26, 1929 PUBLISHED MAY 8, 1930

The butenes are the simplest unsaturated hydrocarbons which exist in isomeric as well as stereoisomeric forms, *viz.*, 1-butene, cis-2-butene, *trans*-2-butene and isobutene. The variety of isomeric changes which they might conceivably undergo in passing from one form to another would include: (1) stereoisomeric change, for example, cis- to trans-2-butene, or vice versa; (2) shifting of the double bond, 1-butene or 2-butene, or vice versa; and (3) shifting of a methyl group, isobutene to 1- or 2-butene, or vice versa. A study of the transformations of these comparatively simple olefins would presumably be of value in the study of the higher olefins.

Before undertaking an investigation on the effect of subjecting the isomeric butenes to different treatments, it was first necessary to develop a satisfactory method of analyzing mixtures containing any combination of these four hydrocarbons. For this purpose the analysis of mixtures of the three normal butenes, *viz.*, 1-butene, cis-2-butene and trans-2-butene

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[1] This paper contains results obtained in an investigation listed as Project 14 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] American Petroleum Institute Research Assistant.

[3] Director, Project 14, American Petroleum Institute.

would serve the purpose since isobutene can apparently be removed by absorption methods.[4] Moreover, the dibromide of this hydrocarbon has a boiling point some 10° lower than any of the others and in the proposed method it could be separated out by fractional distillation. Fortunately this hydrocarbon would not be present in many of the mixtures, especially those being studied at first, and for that reason also the analysis of the normal butenes serves our purpose.

Besides the fractional distillation of the corresponding dibromides, no method for analyzing mixtures of the three normal butenes has appeared in the literature.

The Analytical Method

The method herein developed depends upon the fact that each of the three normal butenes is quantitatively converted into a pure dibromide on treatment with bromine, and each of these dibromides has a different second-order reaction rate with potassium iodide in methanol at 75° to form potassium bromide, free iodine and an unsaturated hydrocarbon, thus: $C_4H_8Br_2 + 2KI \longrightarrow C_4H_8 + 2KBr + I_2$. Since these rates are not symbatic with the boiling points of the dibromides, while the physical properties of density and refractive index are, a combination of rate with one of these properties suffices for the analysis of any mixture of these three dibromides, and therefore of the three normal butenes. For this purpose the densities proved to be more useful than the refractive indices, since they differ by larger amounts.

In Table I are shown the boiling points of the three normal butenes[5] and the boiling points, densities, refractive indices and reaction rate constants of the corresponding dibromides. The rates with which these dibromides react with potassium iodide are proportional to the first power of both the dibromide and potassium iodide concentrations and are therefore second-

TABLE I

PHYSICAL CONSTANTS

Hydrocarbon			Corresponding dibromide						
					Density *in vacuo*		Refractive index		Second-order rate with KI
Name	B. p., °C. (corr.)	Mm.	Name	B. p. at 50.0 mm., °C.	d_4^{25}	d_4^{20}	n_D^{25}	n_D^{20}	
1-Butene	−6 7 to −6 5	748	1.2-dibromobutane	80.5–80.7	1.7870	17951	1 5125	1 5150	0.0765
Cis-2-butene	+2.95 to +3.05	746	Racemic 2,3-dibromobutane	75.6–75 8	1.7836	1.7916	1.5125?	1 5147	0 0297
Trans-2-butene	+0 3 to 3.0.4	744	Meso-2,3-dibromobutane	72.7–72 9	1.7747	1.7829	1.5092	1.5116	0 0544

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[4] (a) Michael and Brunel, *Am. Chem. J.*, **41**, 135 (1909); (b) Konowaloff, *Ber.*, **13**, 2395 (1882); *cf.* Butlerow, *ibid.*, *9*, 77 (1878); (c) Davis, THIS JOURNAL, **50**, 2780 (1928); (d) Davis and Schuler, *ibid.*, 52, 721 (1930).

[5] (a) Lucas and Dillon, *ibid.*, **50**, 1460 (1928); (b) Young, Dillon and Lucas, *ibid.*, *51*, 2528 (1929).

order. The discussion of the order of the reaction is taken up later on in this paper.

The rate with which iodine is formed when a mixture of the three dibromobutanes reacts with potassium iodide is given by Equation 1

$$\frac{dc}{dt} = k_{2a}(C_a)(C_{KI}) + k_{2b}(C_b)(C_{KI}) + k_{2c}(C_c)(C_{KI}) \tag{1}$$

in which C_a, C_b and C_c are the molal concentrations of the three dibromobutanes, A, B, C and k_{2a}, k_{2b}, k_{2c} are the respective second-order reaction constants of the pure components with potassium iodide. This expression is the summation of the three individual rates typified by Equation 2

$$\frac{dc}{dt} = k_{2a}(C_a)(C_{KI}) \tag{2}$$

and is true if the reaction rates are additive. Integration of (1) would give an expression by means of which the progress of the reaction could be followed for any mixture at any time, t, by a determination of the amount of iodine formed. However, the awkwardness of this integration makes it desirable to use instead a simpler expression by means of which an approximation to the real rate can be obtained. Equation 1 may be written in another form (Equation 3)

$$\frac{dc}{dt} = (k_{2a}x + k_{2b}y + k_{2c}z)C_{KI}\ C \tag{3}$$

where x, y and z are the respective molal fractions of A, B and C and ΣC is the total concentration of the dibromides. Setting

$$K_2 = k_{2a}x + k_{2b}y + k_{2c}z \tag{4}$$

Equation (3) becomes

$$\frac{dc}{dt} = K_2C_{KI}\ \Sigma C \tag{5}$$

In Equation 5 K_2 occupies formally the position of a second-order reaction rate constant; it is, however, not constant, because each dibromide disappears at a different rate due to the fact that k„ k_{2b} and k„ have different values, with the consequence that the molal fractions change with time. The rate of change of the molal fractions will depend upon the individual constants k_{2a}, k_{2b} and k_{2c} and will be small when these are of the same order of magnitude. Since this is true in the present case, the mole fractions and hence the value of K_2 will not undergo much change during a not too great interval of time. Accordingly, for experiments in which the reaction is not allowed to proceed too far, Equation 5 may be integrated under the assumption of constancy of K_2, and the value of K_2 taken as that corresponding to the initial molal fractions. K_2 is designated as a "pseudo" second-order reaction rate constant since it is not a true constant.

Assuming that the density of a mixture of the three dibromides may be obtained additively, their relationship may be expressed by Equation 6

$$D = d_ax + d_by + d_cz \tag{6}$$

in which D is the density of the mixture, while d_a, d_b and d_c are the densities of the respective components, A, B and C. Combining 4 and 6 with the additional Equation 7

$$x + y + z = 1 \tag{7}$$

the following solutions for the unknowns are obtained by means of determinants

$$x = \frac{-k_{2b}(d_c - D) + k_{2c}(d_b - D) - K_2(d_b - d_c)}{\Delta} \tag{8}$$

$$y = \frac{k_{2a}(d_c - D) - k_{2c}(d_a - D) + K_2(d_a - d_c)}{\Delta} \tag{9}$$

$$z = \frac{-k_{2a}(d_b - D) + k_{2b}(d_a - D) - K_2(d_a - d_b)}{\Delta} \tag{10}$$

where A $= k_{2b}(d_a - d_c) - k_{2c}(d_a - d_b) - k_{2a}(d_b - d_c) = 0.0005004$.

The assumption that the density of the mixture is an additive function of the individual densities, d_a, d_b and d_c, and that its specific reaction rate constant, K_2, is also an additive function of the individual constants k_{2a}, k_{2b} and k_{2c} would appear to be warranted in view of the fact that halogen compounds of this type are non-polar, non-associated liquids, mixtures of which would presumably deviate but little from ideal solutions.[6]

This method of calculating compositions, besides involving the above assumptions, requires that Equations 4, 6 and 7 should be independent of one another or, in other words, the proportionality constants should not be related in the following way

$$k_{2a} : k_{2b} : k_{2c} = d_a : d_b : d_c$$

Moreover, greater accuracy is realized by the fact that these constants are not symbatically related, that is, the higher-boiling 2,3-dibromide has a higher density but a lower reaction rate than the lower-boiling 2,3-isomer, while the 1,2-dibromide has the highest boiling point, density and reaction rate.

The deviations of approximately 1% in the rate constants of the pure compounds and the error involved in the calculations of the pseudo constant, K_2, determine the maximum error, which appears to be approximately 4% (see Tables VII and IX).

The Reaction Rates

Of the many compounds with which the dibromides react, for example, potassium iodide, sodium thiosulfate, sodium phenolate, potassium cyanide, silver nitrate, ammonia and substituted ammonias, the reactions with the first two only were studied. In all cases except with potassium iodide the amount of material reacted would be obtained from the difference between two much larger quantities while in this case the extent of the reaction can be determined directly and with less error from the amount of iodine formed.

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[6] A mixture of ethylene bromide and propylene bromide is an ideal solution. **Zawidzki**, *Z. physik. Chem.*, *35*, 129 (1900).

The reaction with sodium thiosulfate was carried out in sealed tubes at 100°, preliminary experiments having shown that the rate was too slow at lower temperatures.[7] The reaction as carried out under these conditions is subject to two sources of error: the final titration of the excess of unused thiosulfate varies on the one hand with the gaseous volume above the reacting solution in the sealed tubes and on the other hand with the length of time the unopened reaction tubes stand after removal from the thermostat. Perhaps these errors are not significant at lower temperatures and therefore need not be considered, but they are interfering factors when the reaction is carried out at a temperature of 100°. A fairly satisfactory second-order constant was obtained in the reaction of thiosulfate with pure 1,2- and a mixed 2,3-dibromobutane, but because of the difficulty involved this method was not as suitable as the reaction with potassium iodide.

The reaction rates of alkyl chlorides with potassium iodide in absolute acetone have been studied by Conant and Kirner[8] and Conant and Hussey,[9] who found that the reactivities of the alkyl chlorides decrease in the order, primary, secondary and tertiary. The reaction rates of many dibromo-substituted compounds with potassium iodide have been investigated by Biilmann[10] and by van Duin.[11] Biilmann worked in dilute sulfuric acid solution and van Duin in both 70% ethanol and 70% ethanol acidified with hydrochloric acid. The reaction proceeds differently with the two classes of compounds, an alkyl chloride forming an alkyl iodide and potassium chloride, a dibromide forming an unsaturated compound, iodine and potassium bromide. Van Duin[11b] observed a difference in the reactivities of stereoisomeric dibromides, mesodibromosuccinic acid having a much higher rate than the racemic form. The three dibromobutanes (Table I) would thus be expected to differ in their rates, since the 1,2-dibromide contains a primary bromine atom, more reactive than a secondary, and the isomeric 2,3-dibromides exist as meso and racemic forms.

There are several mechanisms by which the reaction of potassium iodide with these dibromides may proceed, as shown by Equations 11 to 13 inclusive.

$$C_4H_8Br_2 + KI \longrightarrow C_4H_8BrI + KBr \tag{11a}$$

$$C_4H_8BrI + KI \longrightarrow C_4H_8I_2 + KBr \tag{11b}$$

$$C_4H_8I_2 \longrightarrow C_4H_8 + I_2 \tag{11c}$$

$$C_4H_8Br_2 + KI = C_4H_8BrI + KBr \tag{12a}$$

$$C_4H_8BrI + KI = C_4H_8 + I_2 + KBr \tag{12b}$$

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[7] Slator [*J. Chem. Soc.*, *85, 1286 (1904); 87, 481* (1905)] studied the reaction of sodium thiosulfate with ethylene halides at temperatures ranging from *25* to 60°.

[8] Conant and Kirner, THIS JOURNAL, *46,232 (1924).*

[9] Conant and Hussey, *ibid., 47,476 (1925).*

[10] Biilmann, *Rec. trav. chim., 36, 319 (1916).*

[11] *(a)*Van Duin, *ibid., 43,341 (1924)*; *(b)* van Duin, *ibid., 45,345 (1926)*; (c) Kruyt and van Duin, *ibid., 40,258 (1921).*

$$C_4H_8Br_2 + 2KI = C_4H_8I_2 + KBr \tag{13a}$$
$$C_4H_8I_2 = C_4H_8 + I_2 \tag{13b}$$

In addition to the steps enumerated above, each process may, and probably does, involve to some extent the reaction of iodine with potassium iodide as given in Equation 14

$$I_2 + KI = KI_3 \tag{14}$$

In general, the rate will be second order if expressed by (11) and (12), and third order if by (13), provided the reactions of the different steps proceed with markedly different rates. In (11) and (12) the slow reaction may be either (a) or (b), and in (13) it must be (a), since Slator[12] found that diiodides and iodobromides in the presence of iodide ion dissociate quite rapidly even at temperatures of 25 and 35°. It is not possible to establish the extent to which iodine and potassium iodide react according to Equation (14) since in methanol part of the iodine is probably combined with the solvent. Moreover, even though KI_3 is formed, its effect upon the reaction rate can be made negligible by keeping the ratio of potassium iodide to iodine large.

In the experimental work the concentrations of both the reactants were varied. The rate was found to be second order, and to be proportional to the first power of the concentration of both the potassium iodide and dibromobutane. The reaction may then be represented by (11) or (12), but not by (13). This is in accordance with the observations of Biilmann, who studied the behavior of dibromopropionic acid with potassium iodide, but is not in agreement with those of van Duin, who concluded that this reaction and other similar ones were third order, according to Equation 13.

The specific second-order rate constant of a pure dibromide, k_2 (Equation 15), is derived from the differential form (Equation 16).

$$k_2 = \frac{2.303}{t(a - 2b)} \log_{10}\left(\frac{b(a/b - 2\phi)}{a(1 - \phi)}\right) \tag{15}$$
$$dc/dt = k_2(C_{KI})(C_{C_4H_8Br_2}) \tag{16}$$

The third-order constant, k_3 (Equation 17), given for comparison in Tables II, III and IV, is derived from the differential form (Equation 18).

$$k_3 = \frac{1}{t(a - 2b)^2}\left[2.303 \log_{10}\left(\frac{b(a/b - 2\phi)}{a(1 - \phi)} - \frac{2\phi(a - 2b)}{a(a/b - 2\phi)}\right)\right] \tag{17}$$
$$dc/dt = k_3(C_{KI})^2(C_4H_8Br_2) \tag{18}$$

In these equations t is time in hours, a is initial concentration of potassium iodide in moles per liter at 20°, b is initial concentration of dibromobutane in moles per liter at 20° and ϕ is fraction of the total dibromobutane which had reacted at the time, t. The values of k_2 and k_3 are thus expressed in hours and moles per liter at 20°, rather than in hours and moles per liter at 75°. This is done because the solutions are made up at 20° and the concentrations (a) and (b) would each differ at the two temperatures by a factor which is proportional to approximately the cubical coefficient of ex-

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[12] Slator, *J. Chem. Soc.*, **85, 1697 (1904).**

pansion of methanol. Since the ratio of two concentrations occurs in each of the variable terms involving ϕ, the values of k_2 in moles per liter at 20° and of k_2 in moles per liter at 75° are each constant in themselves and differ from each other by this factor. Likewise the values of k_3 at the two temperatures are each constant in themselves but differ from each other by the square of this factor.

The pseudo second-order reaction constant, K_2, of mixtures is also calculated according to Equation 15.

Description of the Method

Materials.—The potassium iodide, "P. W. R. Analytical," was ground in an agate mortar to a powder, dried at 100° for twenty-four hours and kept in a desiccator until used. The sodium thiosulfate solution, 0.02 *N*, was made by dissolving "P. W. R. Analytical" material in distilled water and was allowed to stand some time before use. It was stored in the dark and standardized at frequent intervals against standard potassium dichromate.

The three dibromobutanes used for the reaction rate measurements were those prepared from pure 1-butene,[5a] cis-2-butene and *trans*-2-butene.[5b] The dibromides were fractionally distilled at 50 mm., the products boiling completely within a temperature range of 0.2" (Table I), indicating that each was a pure substance and not a mixture of isomers.

The synthetic methanol used as the solvent was purified by refluxing with sodium hydroxide and distilling from the solid. Water was subsequently added in order to bring the strength to 99.00%. It was not considered feasible to work with absolute methanol since the specific reaction rates are markedly affected by the addition of water to methanol, being much greater at a dilution of 75% than at 99%. Thus the accidental addition of traces of water to absolute methanol might produce greater effects than a slight variation in the composition at 99.00%.

The methanol as prepared usually contained a slight amount of impurity which reacted slowly with iodine at 75°. It was therefore necessary to determine the correction for this impurity by adding to the solvent definite amounts of iodine and potassium iodide equivalent to those encountered in the actual rate measurements and measuring the iodine decrease against time. These corrections, which for three different samples of methanol amounted to 0.00, 1.10 and 1.27 ml. of 0.02 *N* sodium thiosulfate per 20 ml. of solvent, were added to the titration values as determined in the different rate measurements.

Apparatus.—The reaction tubes were made by drawing out very thin glass test-tubes, previously cleaned and dried, to form a constriction near the end. They had capacities slightly greater than 20 ml. A thermostat suitable for carrying on reactions in the dark was maintained at 74.93 ± 0.03".

Procedure.—Each solution containing the reactants was made up to exactly 250 ml. at 20.0°, thoroughly mixed and pipetted into 8 or 10 reaction tubes with a 20-ml. pipet (exact volume, 19.94 ml.). Great care was exercised in keeping the solutions at exactly 20° while being made to volume and while being pipetted, since methanol has a large coefficient of expansion. The tubes were then sealed and placed in the thermostat, care being taken to avoid a large temperature drop by increasing the voltage of the continuous heater just before inserting the tubes. Tubes which were allowed to stand at room temperature for several hours showed no signs of reaction. The time could be considered from the time of immersion. At various intervals tubes were removed from the thermostat, quickly cooled in ice water and broken into a 600-ml. beaker containing 75 ml. of distilled water, 2 g. of potassium iodide and about three-fourths of the amount of sodium thiosulfate solution required for the titration. Thiosulfate was then added until the end-point as indicated with starch was reached. Reaction rate constants were then calculated from the titration values and are shown in the tables.

The densities of the dibromobutanes were determined with a 10-ml. pycnometer. The values have been calculated to vacuum[13] by applying the equation: $d_4^t = \frac{w_l}{w_w}(d_w - \sigma_2) + \sigma_3$. Here $\sigma_2 = \sigma_3 = 0.0012$ and the temperature of w_l and w_w are the same. Densities of the pure compounds are shown in Table I and of mixtures in Table VIII.

Results

In the tables which list the reaction rates, the following notations are used: KI is initial concentration of potassium iodide in moles/liter at 20° (given by "a" in the rate expressions, Equations 15 and 17), $C_4H_8Br_2$ is initial concentration of dibromobutane in moles/liter at 20° (given by "b" in the rate expressions), t is time in hours, ϕ is fraction of dibromide used up at time t, and k_2 and k_3 are second-order and third-order specific reaction constants.

In the experiments represented by Tables II, III and IV, essentially the same dibromide concentration was used throughout and essentially two different concentrations of potassium iodide, the ratio between these last two being approximately 1.5 to 1. In each table the second-order constants calculated for the two potassium iodide concentrations are in satisfactory agreement, whereas the third-order constants are not. This shows that the rates are proportional to the first power and not the second power of the potassium iodide concentration. Since ,previous work on other dibromides by investigators[10,11] had shown the rate to be proportional to the first power of the dibromide concentrations, and since preliminary work on the three dibromobutanes confirmed this observation, as was to be expected, evidence for this conclusion is not given here.

TABLE II

REACTION RATE OF 1,2-DIBROMOBUTANE WITH POTASSIUM IODIDE IN 99.0% METHANOL AT 74.93°

KI, 0.2298 *M*; $C_4H_8Br_2$, 0.03428 *M*				KI, 0.1470 *M*; $C_4H_8Br_2$, 0.03397 *M*			
Time	ϕ	k_2	k_3	Time	ϕ	k_2	k_3
12.50	0.1940	0.0774	0.347	12.50	0.1302	0.0784	0.552
15.50	.2334	.0775	.351	15.50	.1585	.0787	.556
19.25	.2794	.0775	.354	19.00	.1879	.0779	.555
23.75	.3307	.0778	.358	23.75	.2303	.0793	.572
27.25	.3647	.0771	.357	27.25	.2516	.0771	.559
37.50	.4587	.0772	.365	37.50	,3279	.0785	.583
40.75	.4835	.0769	.365	40.75	.3505	.0790	.591
	Average	,0773	.357		Average	.0784	,567

Percentage variation from the mean: $k_2 = 0.6\%$, $k_3 = 22.8\%$.

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[13] Reilly, Rae and Wheeler, "Physico-Chemical Methods," D. Van Nostrand Co., New York, 1925, p. 322.

TABLE III

REACTION RATE OF RACEMIC 2,3-DIBROMOBUTANE WITH POTASSIUM IODIDE IN 99.0% METHANOL AT 74.93°

KI, 0.2327 *M*; $C_4H_8Br_2$, 0.02612 *M*

Time	ϕ	k_2	k_3
11.00	00721	0.0296	0.128
15.42	.0994	.0295	.128
21.50	.1343	.0293	.127
31.75	.1928	.0297	.130
35.50	.2114	.0295	.129
41.67	.2454	.0299	.132
45.50	.2638	.0299	.132
54.75	.3074	.0300	.134
	Average	.0294	.130

KI, 0.1498 *M*; $C_4H_8Br_2$, 0.02785 M

Time	ϕ	k_2	k_3
11.00	0.0500	0.0313	0.212
15.42	.0683	.0309	.209
21.33	.0903	.0301	.204
31.75	.1318	.0304	.208
35.50	.1462	.0305	.210
41 67	.1693	.0306	.212
	Average	.0306	.209

Percentage variation from the mean: $k_2 = 2.0\%$, $k_3 = 23.5\%$.

TABLE IV

REACTION RATE OF MESO-2,3-DIBROMOBUTANE WITH POTASSIUM IODIDE IN 99.0% METHANOL AT 74.93°

KI, 0.2217 *M*; $C_4H_8Br_2$, 0,03287 *M*

Time	ϕ	k_2	k_3
11.50	0.1262	0.0541	0.249
14.50	.1552	.0539	.249
17.50	.1837	.0539	.250
21.00	,2173	.0545	254
27.75	.2759	.0549	.259
36.50	.3416	.0547	.261
39.50	.3627	.0547	.261
43.17	.3853	.0543	.261
	Average	.0544	.256

KI, 0.1461 *M*; $C_4H_8Br_2$, 0.02629 *M*

Time	ϕ	k_2	k_3
11.50	0.0848	0.0539	0.375
14.50	.1063	.0542	.378
17.50	.1259	.0540	.379
21.00	.1515	.0551	.389
27.75	.1952	.0557	.396
36.50	.2440	.0551	.396
	Average	.0545	.386

Percentage variation from the mean: $k_2 = 0.1\%$, $k_3 = 20.2\%$.

In determining the dependence of the specific reaction constant on the concentration of potassium iodide it was necessary to decrease this concentration to somewhat lower values than those ordinarily employed in the rate measurements. Thus under these conditions the ratio of the concentration of potassium iodide to dibromide was small compared to the usual values. With a ratio above 6.0, the values of the specific reaction constants were independent of this ratio in so far as investigated (that is, up to 12.0), but below 6.0 the specific reaction constants were found to increase slightly. This effect although quite small is very definite since it invariably occurred when the ratio was low; for example, the values for a given sample of dibromide were 0.0364 and 0.0365 when the ratios were 9.44 and 8.32, respectively, but 0.0381 when the ratio was 4.29.

Table V shows the iodine correction for one sample of methanol. Because of the low rate it was not possible to apply this correction before twenty hours; consequently in the rate determinations of the dibromides, readings taken under twenty hours are in error. Table VI shows that this iodine correction does not affect the second order rate constant.

TABLE V

REACTION OF METHANOL WITH IODINE

Time in hours	0.00	11.42	21.17	36.33
0.02 N I_2 reacted, ml.	0.00	1.23	1.27	1.27

TABLE VI

EFFECT OF IODINE CORRECTION UPON REACTION RATE

Methanol	1	2	3	4
Iodine correction	0.00	0.45	1.10	1.27
Second-order constant	0.0761	0.0769	0.0773	0.0766

The specific second-order reaction rates of the pure dibromides are summarized in Table VII.

TABLE VII

REACTION RATES OF PURE DIBROMOBUTANES WITH POTASSIUM IODIDE IN 99.0% METHANOL AT 74.93°

Mean values from different runs at slightly varying concentrations

Material	Run	No. of exptl. detns. of k_2	k_2	Mean k_2	Deviation from the mean, %
1,2-Dibromobutane, a	23	5	0.0773		+1.05
b	32	7	.0761	0.0765	−0.52
b	34	6	.0766		+ .13
a	45	8	.0761		− .52
Racemic 2,3-dibromobutane	27	6	.0297	.0297	+ .17
	42	6	.0296		− .17
Meso-2,3-dibromobutane	21	6	.0544		.00
	22	5	.0545		+ .18
	38	6	.0541	.0544	− .55
	39	8	.0540		− .73
	41	6	.0550		$1.10

The two samples, a and b, were prepared from different samples of 1-butene.

The satisfactory agreement in the case of the two samples of the 1,2-dibromide shows that the experimental conditions can be duplicated. This is likewise demonstrated by' the fact that two of the authors (R. T. Dillon and W. G. Young) obtained for each of the three compounds constants which are essentially identical.

When the method was applied to different mixtures of the dibromobutanes satisfactory pseudo second-order constants were obtained as shown in Table VIII.

The compositions of these mixtures are given in Table IX. Duplicate runs were made on Mixtures B and D, the less satisfactory result in each case being shown in Table VIII.

In Table IX these observed values of the pseudo constant K_2 are compared with the values calculated from the known constants of the com-

TABLE VIII

REACTION RATES OP DIBROMOBUTANE MIXTURES WITH POTASSIUM IODIDE IN METHANOL AT 74.93°

Mixture	A			B	
KI concn.	0 02283 molal			0 1484 molal	
$C_4H_8Br_2$ concn.	0 02054 molal			0.01734 molal	
Time	ϕ	ke	Time	ϕ	k_2
32.00	0.3280	0.0562	16.25	0.1429	0.0652
33.00	.3382	.0566	19.50	.1683	.0650
34.92	.3548	.0568	22.50	.1914	.0652
36.42	.3655	.0567	25.83	.2169	.0651
38.17	.3765	.0554	28.75	.2377	.0656
40.33	.3931	.0564	34 00	.3074	.0660
	Average	0.0566			0.0653

Mixture	C			D	
KI concn	0 2291 molal			0 2284 molal	
$C_4H_8Br_2$ concn.	0.0254 molal			0.02611 molal	
Time	ϕ	k_2	Time	ϕ	k_2
18.00	0 2052	0 0571	24 72	0 2216	0.0457
20.50	.2311	.0576	28.28	.2536	.0468
23.50	.2619	.0583	31.50	.2767	.0467
26.50	2903	0584	41.75	.3463	.0467
29.50	,3175	0587	44.00	.3588	.0463
39.75	.3953	.0585	46.50	.3739	.0463
41.75	.4105	.0582	48.25	.3825	.0460
43.75	.4233	.0579	50.16	.3928	.0459
46.00	.4389	.0558?	53.42	.4116	.0459
47.75	.4494	.0578			
	Average	0 0583			0.0462

ponents. In all cases the observed values are low, a result which is not surprising since K_2 should presumably decrease as the molal fraction ratio of the pure dibromobutanes changes. The percentage of the 1,2-dibromobutane is in all cases low, the maximum deviation being about 4%.

TABLE IX

REACTION RATES, DENSITIES AND CALCULATED COMPOSITIONS OF DIBROMOBUTANE MIXTURES

	Component			Dibromobutane mixture					
			d_4^{25}	% composition by		"Pseudo" constant K_2		Density in vacuo, d_4^{25}	
Mixture	Substance	k_2	in vacuo	Wt.	Anal.	Calcd.	Obs.	Calcd.	Obs.
A	1,2-Dibromobutane, pure	0 0765	1.7870	45 06	42 0				
	2,3 Dibromobutane, mixed	0365	1 7816	35 81	39 6	0 0590	0.0566	1 7827	1 7826
	2,3-Dibromobutane, pure	0544	1 7747	19 13	18 4				
B	1,2-Dibromobutane, pure	0765	1 7870	79 38	77 4, 76 1	0668	,0659		
	2,3-Dibromobutane, pure	,0297	1 7836	20 62	22 6, 23 9		.0653		
C	1,2-Dibromobutane, pure	.0765	1 7870	58 57	54 6	.0599	.0583		
	2,3-Dibromobutane, mixed	.0364	. . .	41 43	45 4				
D	1,2-Dibromobutane, pure	.0765	1.7870	26 53	23 2, 24 4	.0470	.0457		
	2,3-Dibromobutane, mixed	.0364	. . . .	73 47	76.8, 75 6		.0462		
E	1,2-Dibromobutane, pure	,0765	1 7870	57 53	55 9			1.7828	1 7829
	2,3-Dibromobutane, mixed	. . . .	1 7777	42 47	44.1				

In order to conserve the limited supply of the pure 2,3-dibromobutanes, mixtures of these two isomers resulting from fractional distillation were generally used in place of the pure compounds.

Rate measurements with the pure dibromobutanes were made at 59.72'. From the results at the two temperatures the heats of activation, Q, and the temperature coefficients were calculated by means of the Arrhenius equation. The values are given in Table X.

TABLE X

TEMPERATURE COEFFICIENTS AND HEATS OF ACTIVATION

Dibromobutane	k_2 59.72°	k_2 74.93°	Heats of activation, cal.	Temp. coeff. for 10° $\frac{69.72°}{59.72°}$	Temp. coeff. for 10° $\frac{74.93°}{64.93'}$
1,2-	0.0147	0.0765	24,900	3.01	2.91
2,3-meso-	.00896	.0544	27,300	3.33	3.22
2,3-racemic	.00462	.0297	28,100	3.46	3.34

Summary

The specific reaction rates of 1,2-dibromobutane and of racemic and meso-2,3-dibromobutane with potassium iodide in methanol have been measured at 60 and at 75°. They are second-order reactions. The heats of activation and temperature coefficients have been calculated.

The reaction rates of mixtures of these dibromides have likewise been measured at 75°. Calculation of the composition of binary mixtures from the reaction rates and of a ternary mixture from the reaction rate and density gave results in satisfactory agreement with the known compositions. The maximum deviation was 4%.

Mixtures of the three normal butenes may be analyzed by first converting them to the corresponding dibromides and determining for these the reaction rates and densities.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 242]

THE COMPOSITION OF BUTENE MIXTURES RESULTING FROM THE CATALYTIC DECOMPOSITION OF THE NORMAL BUTYL ALCOHOLS

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Introduction

Within recent years considerable interest has been attached to the decomposition of the normal butyl alcohols, partly because of its importance as a source of butenes and partly because of its bearing upon the theory of catalysis. These decompositions would be of particular value if they should yield, under the proper conditions, pure butenes, rather than mixtures of these hydrocarbons.

The catalytic decomposition of 1-butanol was first accomplished by Le

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[1] Du Pont Fellow in Chemistry, 1928–1929.

Bel and Green,[2] who dropped the alcohol upon hot zinc chloride. The alcohol has also been dehydrated by passing the vapor over a variety of catalysts at elevated temperatures.[3] The catalytic dehydration of 2-butanol has likewise been accomplished in different ways.[3n,o,4]

The composition of the butene mixtures obtained in the decompositions of these alcohols depends to a considerable extent upon the catalyst used and in most cases has been reported as being 1-butene, 2-butene, or a mixture of these. The isobutene present in some of these mixtures, as reported by a few investigators,[3a,c,e,4a] probably arose from isobutanol in the alcohol used, as was actually demonstrated in one case.[4a] The methods which have been used for analyzing mixtures of 1- and 2-butene, except those which depend upon a separation of the corresponding dibromobutanes[2,3f,l,o] in general rely upon a difference in the reactivity of 1-butene and 2-butene. Since, however, there are two isomeric 2-butenes, it is evident that any method developed on the assumption that a mixture of the 2-butenes behaves as a pure compound lacks accuracy and consequently the results obtained by it are in error.[3n,5] This criticism, however, does not apply to the ozonide method,[4b,c] which distinguishes between 1-butene and the mixed 2-butenes.

TABLE I

THE CATALYTIC DECOMPOSITION OF THE NORMAL BUTYL ALCOHOLS

No.	Alcohol	Catalyst	Temp., °C.	Duration of run min.	Alcohol Used, *g.*	Recovered, *g.*
1	1-Butanol	H_2SO_4 60%	140–160	...	74	..
2	2-Butanol	H_2SO_4 60%	115–140	...	74	..
3	2-Butanol	H_3PO_4 85%	95–126	...	148	..
4	1-Butanol	P_2O_5	100–140	...	74	..
5	2-Butanol	P_2O_5	90–130	...	74	..
6	1-Butanol	H_3PO_4 on pumice	390–400	105	80	..
7	2-Butanol	H_3PO_4 on pumice	340–345	78	60	0
8	1-Butanol	$AlPO_4$	440–450	87	72	24
9	2-Butanol	$AlPO_4$	340–350	81	72	18
10	1-Butanol	Al_2O_3	340–370	80	60	5
11	2-Butanol	Al_2O_3	335–345	125	60	3

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[2] Le Bel and Green, *Am. Chem. J.*, **2**, 24 (1881).

[3] (a) Ipatiew, *Ber.*, 36, 1999 (1905); (b) Sabatier and Senderens, *Ann. chim. phys.*, [8] 4, 458 (1905); (c) Senderens, *Compt. rend.*, 144, 1110 (1907); (d) Sabatier and Mailhe, *Ann. chim. phys.*, [8] 20, 325 (1910); (e) Senderens, *ibid.*, 25, 449 (1912); (f) King, *J. Chem. Soc.*, 115, 1404 (1919); (g) Pease and Yung, THIS JOURNAL, 46, 402 (1924); (h) Adkins and Nisson, *ibid.*, 46, 130 (1924); (i) Brown and Reid, *J. Phys. Chem.*, 28, 1081 (1924); (j) Adkins and Perkins, THIS JOURNAL, 47, 1163 (1925); (k) Lazier and Adkins, *ibid.*, 47, 1719 (1925); 48, 1671 (1926); (l) Lépingle, *Bull. soc. chim.*, 39, 741 (1926); (m) Coffin and Maass, THIS JOURNAL, 50, 1427 (1928); (n) Davis, *ibid.*, 50, 2769 (1928); (o) Lucas, Dillon and Young, *ibid.*, 52, 1949 (1930).

[4] (a) Ipatiew and Sdzitowecky, *Ber.*, 40, 1827 (1907); (b) Harries, *Ann.*, 383, 181 (1911); (c) Harries and Evers, *ibid.*, 390, 238 (1912).

[5] Michael and Brunel, *Am. Chem. J.*, 41, 135 (1909).

TABLE I (Concluded)

		Dibromide mixture				% Composition of butene mixtures				
						By density and reaction rate			By density alone	
No.	Yield on alcohol. %	°C.	Press., mm.	Reaction rate	Density in vacuo d_4^{25}	1-Butene, b. p. −6.7°	2-Butene, b. p. +3.0° *cis*	2-Butene, b. p. +0.3° trans	2-Butene, b. p. +3.0° *cis*	2-Butene, b. p. +0.3° *trans*
1	39.0	74.5–75.8	51.0	0.0466	1.7775	0.1	31.5	68.4	31.5	68.5
2	88.1	73.8–75.5	48.5	.0435	1.7784	−1.1	43.1	58.0	41.6	58.4
3	95.0	73.0–75.6	50.0	.0435	1.7782	−2.1	42.2	59.9	39.4	60.6
4	45.0	74.3–76.5	52.0	.0470	1.7774	0.2	30.1	69.7	30.4	69.6
5	77.0	73.0–75.2	49.0	.0429	1.7783	−2.5	44.0	58.5	40.4	59.6
6	..	73.3–75.5	48.0	.0504	1.7880	19.1	33.2	47.7	..	..
7	85.5	72.3–74.5	47.0	.0485	1.7799	15.2	37.4	47.4	..	..
8	86.0	75.2–78.3	47.7	.0631	1.7829	56.0	14.8	29.2	..	..
9	85.5	73.4–77.5	48.0	.0486	1.7806	18.8	40.3	40.9	..	..
10	80.5	74.0–77.4	47.5	.0668	1.7850	72.9	15.0	12.1	..	..
11	97.7	75.2–78.0	50.0	.0446	1.7824	20.6	58.1	21.3	..	..

The method for analyzing mixtures of 1-butene, cis-2-butene and *trans*-2-butene by means of the densities and the reaction rates of the corresponding dibromides[6] has been applied to the mixtures resulting from the decomposition of 1-butanol and 2-butanol with different dehydrating agents. The results are given in Table I.

Experimental

Materials.—The 1-butanol and 2-butanol were purified as described for other decompositions.[3c,7]

Merck's bromine was shaken with a solution of potassium iodide and distilled from concentrated sulfuric acid.

Columbian spirits, free from acetone, was refluxed with sirupy phosphoric acid for three hours in order to remove traces of amines, and slowly distilled through the column used for purifying the butanols, the first and last portions being discarded. The main portion of the methanol was then refluxed for three hours with flake caustic soda, slowly distilled and the part distilling at 64.2–64.6° (745 mm.) was diluted with water to a density, d_4^{20}, of 0.7945, the density of 99.0% methanol.

The potassium iodide, P. W. R. analytical, was heated to 120° for four hours and placed in a desiccator until used.

The dehydrating agents for the alcohol decompositions were aluminum oxide,[3c] Baker's C. P. aluminum phosphate previously heated to 400°, Merck's phosphorus pentoxide, P. W. R. "highest purity" 85% phosphoric acid, 60% sulfuric acid, made by diluting Baker's C. P. acid, and pumice impregnated with phosphoric acid.

Apparatus.—The decompositions of 1-butanol and 2-butanol with phosphorus pentoxide, phosphoric acid and sulfuric acid were accomplished in a three-necked three-liter flask. The resulting butene was passed in succession through a reflux condenser, a trap at 0°, a 24% solution of perchloric acid contained in a spiral wash bottle, a calcium chloride drying tube and finally into the brominating flask at −15° provided with an outlet attached to calcium chloride and soda lime tubes. The apparatus used for effecting the decompositions over aluminum oxide, aluminum phosphate and pumice

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[6] Dillon, Young and Lucas, THIS JOURNAL, 52, 1953 (1930).

[7] The 2-butanol was kindly supplied by the Stanco Distributors, N. Y., through the courtesy of Mr. C. L. Bowman.

impregnated with phosphoric acid and also the set-up employed in the distillation of the dibromides at 50 mm. were the same as those used for other decompositions.[3o]

Decomposition of the Alcohols.—The rate of decomposition of the alcohols was determined as rapidly as consistent with effective handling of the butene by the purifying train. The procedures used varied with the dehydrating agents. In the case of 60% sulfuric acid and 85% phosphoric acid, the alcohols and acid were heated together in the generating flask in the following proportions: 220 g. of 60% sulfuric acid with 74 g. (1.0 mole) of alcohol, 475 g. of 85% phosphoric acid with 148 g. (2 moles) of alcohol.[3n] The decomposition of 2-butanol proceeds the more readily. In the case of phosphoric acid no butene could be obtained from 1-butanol, even with the addition of diatomaceous earth.

The alcohols were dropped onto the phosphorus pentoxide in the following proportions: 74 g. (1.0 mole) of 1-butanol or 118 g. (1.6 moles) of 2-butanol[4b] upon 100 g. of phosphorus pentoxide.

In the case of aluminum oxide, aluminum phosphate and phosphoric acid on pumice the decompositions were effected in the usual manner.[3o] Of the last three catalysts, aluminum oxide was the most effective and the aluminum phosphate was decidedly inferior to the other two. Here also the 2-butanol was the more easily decomposed. The yield was calculated from the amount of alcohol decomposed, obtained by subtracting the amount recovered from that put through the furnace.

Purification of the Dibromobutanes.—The crude dibromides contained small amounts of lower-boiling impurities but no higher-boiling ones, such as tribromobutane. In every case the low-boiling impurity was removed by conducting the first part of the distillation at a very slow rate and removing in the first fraction about 10% of the total weight of the dibromides. The range of this fraction was usually three or four degrees and of this material about 90% came over at the top of its boiling range. The necessity of removing this first fraction was indicated by the analysis of the binary mixture of isomeric 2-butenes obtained in the decomposition of 2-butanol with phosphoric acid. A marked discrepancy was found between the reaction rate and the density of the resulting 2,3-dibromobutanes following one distillation at 50 mm. without fractionation. The separation effected by a subsequent fractional distillation was indicated by the refractive indices of successive cuts, the values being 1.5097, 1.5128, 1.5129, 1.5130 and 1.5132. After discarding the first fraction, the remaining fractions were combined and density and reaction rate measurements were taken. These values were 1.7775 and 0.0435, respectively, whereas the corresponding values for the material before fractionation were 1.7759 and 0.0435. From these figures it is evident that the impurity was material of low density and not isobutene dibromide, the density of which lies close to that of the 2,3-dibromobutanes. The ratio of the dibromides had not been materially altered by the removal of this first fraction since (1) the reaction rate was not affected, (2) the refractive indices of the other four fractions were about the same and (3) previous attempts at fractional distillation of dibromobutanes had not effected a complete separation even after six fractionations.[3o]

Analysis of the Dibromobutane Mixtures.—From the densities and the reaction rate measurements of the dibromobutane mixtures with potassium iodide in methanol, the percentage of 1-butene, cis-2-butene, b. p. 3.0°, and trans-2-butene, b. p. 0.3°, in the original butene mixture can be calculated according to the respective equations

$$X = \frac{-K_{2b}(d_c - D) + k_{2c}(d_b - D) - K_2(d_b - d_c)}{\Delta}$$

$$Y = \frac{k_{2a}(d_c - D) - k_{2c}(d_a - D) + K_2(d_a - d_c)}{\Delta}$$

$$Z = \frac{-k_{2a}(d_b - D) + k_{2b}(d_a - D) - K_2(d_a - d_b)}{\Delta}$$

in which k_{2a}, k_{2b} and k_{2c} are the specific second-order constants of the corresponding pure dibromobutanes, d_a, d_b, d_c are their densities, K_2 and D are the observed reaction rate and density of the dibromide mixture and $\Delta = k_{2a}(d_a - d_c) - k_{2c}(d_a - d_b) - k_{2a}(d_b - d_c) = 0.0005004$.

Since the results on known mixtures showed an error of 2 to 4%, it seems reasonable to assume that the maximum error in this method is not greater than 5%.[6] When analysis indicated that the decomposition product was a binary mixture, calculation from the density alone gave results in agreement within the limits specified, as shown in the table.

It should be pointed out that in using this method for the analysis of butene mixtures the purity of the solvent must be checked by running a reaction rate with pure 1,2- or 2,3-dibromobutane.

Discussion

Perhaps the most striking features of the decompositions are the presence of the 2-butenes in all of the reaction products and the absence of 1-butene in the reaction product from both 1-butanol and 2-butanol when phosphorus pentoxide, phosphoric acid or sulfuric acid is used at temperatures below 160°. In all these cases the lower-boiling 2-butene is in excess and its amount is largest from 1-butanol. The behavior of 2-butanol with the pentoxide is in agreement with the results of Harries and Evers,[4c] who found that no 1-butene was present although they made no distinction between the isomeric 2-butenes. The decomposition of 2-butanol with phosphoric acid has been carried out by Davis,[3a] who analyzed the butene fraction distilling at 1.5–1.7° by the bromine absorption method and found 84% to be rapidly brominated, therefore 2-butene, and 16% to be slowly brominated, therefore presumably 1-butene. He has misinterpreted his results, having failed to appreciate that the isomeric 2-butenes might absorb bromine at different rates. From our analysis and his bromination experiments it is evident that the lower-boiling (0.3°) isomer has the faster reaction rate with bromine. It is interesting to note that the dibromide of this isomer also has the higher reaction rate with potassium iodide. It is not likely that the composition of the distillate studied by Davis was materially different from that of his original butene mixture since the fraction at 1.5–1.7° is midway between the pure hydrocarbons.[8]

No appreciable quantity of butene was formed when 1-butanol was refluxed with 85% phosphoric acid. The composition of the butene mixtures resulting from the decomposition with 60% sulfuric acid has not been reported previously.

[8] Young, Dillon and Lucas, THIS JOURNAL, 51, 2528 (1929).

Of the higher temperature decompositions in the gas phase, 1-butene was in excess in only two cases, the largest amount coming from 1-butanol over aluminum oxide. Approximately the same quantity of 1-butene was obtained from 2-butanol irrespective of the catalyst. The higher-boiling 2-butene (cis) was in excess over the other two products in only one case, *viz.*, 2-butanol over aluminum oxide; and it was only with this catalyst that the amount of the cis-isomer exceeded that of the trans.

The decomposition of 1-butanol over phosphoric acid on pumice has been reported previously by King[3f] and by Coffin and Maass.[3m] The former found no isobutene and obtained nearly pure 2,3-dibromobutanes on fractionation of the mixed dibromides. The latter, by distillation of both the olefin and its dibromide, obtained 10–15% of 1-butene, the balance being 2-butene. Their result for 1-butene, although somewhat lower than ours, is in substantial agreement. The fraction distilling at 1.0° and believed by them to be pure 2-butene was undoubtedly a mixture.

The composition of the mixture from the decomposition of 1-butanol over aluminum oxide first reported by Ipatiew[3a] has been studied recently by Davis,[3n] Lépingle,[3l] and by Lucas, Dillon and Young.[3o] Davis claimed 65% 1-butene and 35% 2-butene by his bromine absorption method. His result for 1-butene would agree better with ours if correction could be made for the difference in reactivity of the isomeric 2-butenes. The results obtained by Lépingle for 1-butanol and by Lucas, Dillon and Young for 1- and 2-butanol over aluminum oxide agree fairly well with the analyses given in the table, considering the limitations of the distillation method. Lépingle obtained 78% 1-butene and 22% 2-butene for 1-butanol while Lucas, Dillon and Young report 68% 1-butene, 20% higher- and 12% lower-boiling 2-butene. The latter obtained from 2-butanol 26%, 48% and 26%, respectively.

The decomposition of 1-butanol over aluminum phosphate has been reported by Senderens,[3c] who obtained a mixture of 73% 1-butene and 27% isobutene, Since no evidence has been found for the presence of isobutene in any of the decompositions described in this paper, it seems likely that the presence of isobutene in the product reported by Senderens was due to isobutanol in the alcohol used by him.

From the results listed in the table it is evident that neutral dehydrating agents favor 1-butene, whereas the acidic ones favor 2-butene, the order for both alcohols being aluminum oxide, aluminum phosphate, phosphoric acid on pumice and finally the three acidic reagents, phosphorus pentoxide, phosphoric acid and sulfuric acid. The last three likewise favor the lower-boiling 2-butene.

Removal of Bromine from Dibromobutane.—Since bromine adds across the bond, and not on the same side,[9] a study was made of the re-

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[9] Michael, *J. prakt.* Chem., 52,344 (1893); Chavanne, Revue *Générale des Sciences,*

moval of bromine from 2,3-dibromobutane to determine whether the original or the isomeric 2-butene was produced. It was found that the hydrocarbon formed by the removal of bromine from a mixed 2,3-dibromobutane gave, with bromine, a dibromide identical with the original. The removal of bromine therefore appears to be a trans elimination similar to other reactions in which halogens or halogen halides are eliminated.

135.5 *g.* of 2,3-dibromobutane, obtained from the butene resulting from the decomposition of 2-butanol with phosphorus pentoxide and having a second order reaction rate with potassium iodide, K_2, of 0.0430, was allowed to drop upon 77 g. of 10-mesh granulated zinc, P. W. R. C. P. under 110 ml. of ethanol at 80–95°. The evolved butene, after passage through a reflux condenser, was purified as usual and allowed to react with bromine. The purified dibromide, 122.3 g. (90% yield), gave for K_2 the value of 0.0231. It was thus identical, within experimental error, with the original dibromide.

Summary

Decompositions of 1-butanol and 2-butanol have been effected by dropping the alcohols upon phosphorus pentoxide, by heating the alcohols with 85% phosphoric acid and with 60% sulfuric acid and by passing the vapor of the alcohols at high temperatures over aluminum oxide, over aluminum phosphate and over pumice impregnated with phosphoric acid. The butene mixtures were analyzed by converting them to the dibromides and determining for the latter the densities and the reaction rates with potassium iodide in methanol. Both 1-butanol and 2-butanol gave a mixed 2-butene free from 1-butene when the dehydrating agent was phosphorus pentoxide, phosphoric acid or sulfuric acid and the decomposition was carried out below 160°, except, however, that 1-butanol was not decomposed by phosphoric acid. 2-Butanol with phosphoric acid on pumice, with aluminum phosphate, or with aluminum oxide gave largely 2-butene, the amount of 1-butene increasing slightly in the order named. With 1-butanol the amount of 1-butene obtained when these three catalysts were used increased rapidly in the order named, being 73% with aluminum oxide. In general, the more acidic reagents favor trans-2-butene and the less acidic favor I-butene and cis-2-butene.

The removal of bromine with zinc from a mixed 2,3-dibromobutane produced a mixed 2-butene identical in composition with the butene from which the dibromide was prepared.

PASADENA, CALIFORNIA

35, 229 (1924). The cis addition observed by Terry and Eichelberger, THIS JOURNAL, 47, 1067 (1925), was effected in aqueous solution in the presence of bromide ions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

STRUCTURE OF THE SALTS OF AROMATIC NITRILES

BY FRED W. UPSON, ROBERT T. MAXWELL AND HOWARD M. PARMELEE[1]

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In the course of work reported in 1922 from this Laboratory,[2] the impure sodium salt of phenylacetonitrile was isolated. Because of certain properties the authors suggested the nitride structure $(C_6H_5)H{-}C{=}C{=}N{-}Na$ for this substance. It was also suggested that an imide form of the parent nitrile $(C_6H_5)H{-}C{=}C{=}N{-}H$ is an intermediate substance in certain condensation reactions undergoing rearrangement to the nitrile form $((C_6H_5)H{-}\underset{|}{C}{-}C{\equiv}N)H$.

In two papers published recently by Rising and co-workers[3] similar ideas are expressed and the theory concerning tautomerism of the nitriles is more fully developed than in the paper of Upson and Thompson.

Several reactions carried out in this Laboratory favor the nitride structure of the sodium salt.

(I) Decomposition at high temperatures yields stilbene and sodium cyanide.

$$(C_6H_5)H{-}C{=}C{=}N{-}Na \longrightarrow (C_6H_5)H{-}C{=} + NaNC$$
$$2C_6H_5H{-}C{=} \longrightarrow (C_6H_5)H{-}C{=}C{-}H(C_6H_5)$$

(II) An impure silver salt of phenylacetonitrile possessing in all probability the nitride structure was prepared from the sodium salt by interaction with silver nitrate in alcoholic solution. The silver salt on interaction with butyl iodide gave an alkyl derivative of nitride structure, since after decomposition there was isolated butylamine in the form of its hydrochloride.

$$(C_6H_5)H{-}C{=}C{=}N{-}Ag + C_4H_9I \longrightarrow (C_6H_5)H{-}C{=}C{=}N{-}C_4H_9 + AgI$$
$$(C_6H_5)H{-}C{=}C{-}N{-}C_4{-}H_9 \longrightarrow (C_6H_5)H{-}C{=} + C_4H_9{-}N{=}C$$
$$C_4H_9{-}N{=}C + H_2O + HCl \longrightarrow C_4H_9NH_3Cl + HCOOH$$

(III) Spontaneous oxidation of sodium phenylactonitrile in the air leads to the formation of benzoic acid and sodium cyanide

$$(C_6H_5)H{-}C{=}C{=}N{-}Na + O_2 \longrightarrow C_6H_5COOH + NaNC$$

(IV) Toluene and sodium cyanide are formed during the preparation of the salt.

$$2C_6H_5H{-}C{=}C{=}N{-}H + 2Na \longrightarrow 2(C_6H_5)H{-}C{=}C{=}N{-}Na + 2H$$

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[1] Based in part upon theses presented by Robert W. Maxwell and Howard M. Parmelee for the Master of Science degree, University of Nebraska. Presented before the Organic Division of the American Chemical Society at the Minneapolis Meeting, September, 1929.

[2] Upson and Thompson, THIS JOURNAL, 44,181 (1922).

[3] Rising and Zee, *ibid.*, 50, 1699 (1928); Rising, Muskat and Lowe, *ibid.*, 51, 262 (1929).

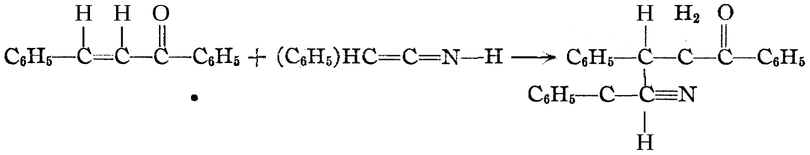
A part of the salt is reduced to toluene and sodium cyanide by the hydrogen liberated in the above reaction.*

$$(C_6H_5)H-C=C=N-Na + H_2 \longrightarrow C_6H_5CH_3 + NaNC$$

This reduction which always accompanies the formation of the sodium salt of phenylacetonitrile explains the difficulty experienced by us and by Rising and co-workers in preparing the pure salt.[5] Unless the sodium cyanide is removed it contaminates the salt of the nitrile. Details of the preparation of the salt in pure form will be found in the experimental part.

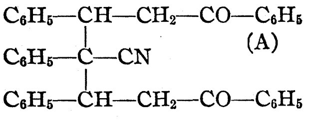
(V) Condensation reactions of the type studied by Avery[6] can be produced by the use of sodium phenylacetonitrile, as well as by the use of sodium methylate and benzyl cyanide.

The work of Avery involves condensation of benzyl cyanide with unsaturated esters and ketones using sodium methylate as the condensing agent. Benzalacetophenone condenses with the sodium phenylacetonitrile in methyl alcohol solution to give a 97% yield of 1,5-dibenzoyl-2,3,4-triphenyl-3-cyanopentane. The same compound is obtained by the use of sodium methylate and phenylacetonitrile



$$C_6H_5-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5 + (C_6H_5)HC=C=N-H \longrightarrow C_6H_5-\overset{H}{\overset{|}{\underset{\underset{C_6H_5-C-\underset{\underset{H}{|}}{C}\equiv N}{|}}{C}}}-\overset{H_2}{C}-\overset{O}{\overset{\|}{C}}-C_6H_5$$

This latter through its imide form gives, with a second molecule of benzalacetophenone, the condensation product 'obtained by Avery (A). This result constitutes evidence that phenylacetonitrile is tautomerized by sodium methylate as well as by metallic sodium since the two methods give theidentical product.



(A)

$$\begin{array}{l} C_6H_5-CH-CH_2-CO-C_6H_5 \\ \qquad | \\ C_6H_5-C-CN \\ \qquad | \\ C_6H_5-CH-CH_2-CO-C_6H_5 \end{array}$$

Rising, Muskat and Lowe[7] have suggested that sodium phenylacetonitrile exists in two forms designated as "carbide" and "nitride." They explain "the behavior of this salt and of its homolog, sodium α-phenylbutyronitrile, in the reactions studied, upon the assumption of nitride–carbide tautomerism, obviously an extension of the Nef theory with regard to the tautomerism of hydrocyanic acid."

According to our interpretation of the behavior of these salt, there exists only the one form, the "nitride." We would explain condensation reac-

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[4] See in this connection von Meyer, *J. prakt. Chem.*, 22,261 (1880).

[5] Zee (Ref. 3) prepared the pure sodium salt of phenylacetonitrile but Rising later was unable to repeat his work. Rising, Muskat and Lowe more recently have prepared the pure potassium salt.

[6] Avery, THIS JOURNAL, 50,2512 (1928).

[7] Rising, Muskat and Lowe, *ibid.*, 51, 263 (1929).

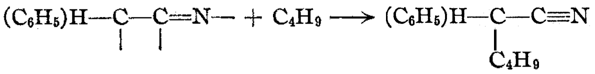
tions of these salts at the carbon atom as involving rearrangement of the anion during the reaction, and condensation at the nitrogen atom as direct replacement of the sodium without rearrangement. Thus just as silver cyanide gives alkyl isocyanides with alkyl halides, so we found that the silver salt of phenylacetonitrile gives a nitrogen derivative on reaction with butyl iodide

$$(C_6H_5)H{-}C{=}C{=}N{-}Ag + C_4H_9I \longrightarrow (C_6H_5)H{-}C{=}C{=}N{-}C_4H_9 + AgI$$

Rising, Muskat and Lowe found that the sodium salt condenses with butyl iodide to give α-phenylbutyronitrile. This we believe involves rearrangement of the anion.

$$(C_6H_5)H{-}C{=}C{=}N{-}Na \longrightarrow (C_6H_5)H{-}C{=}C{=}N{-} + Na^+$$

$$C_4H_9I + Na^+ \longrightarrow C_4H_9{-} + NaI$$



$$(C_6H_5)H{-}\underset{|}{C}{-}\underset{|}{C}{=}N{-} + C_4H_9 \longrightarrow (C_6H_5)H{-}\underset{\underset{C_4H_9}{|}}{C}{-}C{\equiv}N$$

Experimental Part

Preparation of Sodium **Phenylacetonitrile.**—In a 500-cc. flask were placed 4.4 g. of sodium in the form of fine shot and 220 cc. of ether which had been specially dried. The flask, connected to a reflux condenser, was warmed on a hot-plate just sufficiently to cause the ether to boil. Dry phenylacetonitrile (23 g.) was added drop by drop, over a period of one hour and thirty minutes. At the end of this time the contents of the flask consisted of a white solid suspended in a yellow solution. The heating was continued for six hours, at the end of which time the sodium had disappeared. All apparatus was specially dried and the reaction mixture was protected from moisture, oxygen and carbon dioxide during the course of the reaction.

The contents of the flask after cooling to 20° deposited a small quantity of white solid. This was removed by filtration under vacuum in an apparatus designed to exclude air and moisture. The solid weighed 1.2 g. and proved to be sodium cyanide. It gave the usual qualitative tests for the cyanide ion and on analysis was found to contain 47.44% Na; calculated for NaCN, 46.93%.

The sodium phenylacetonitrile precipitated from the ethereal filtrate after standing for several days, in the form of frost-like crystals. The salt was removed by filtration in an atmosphere of dry nitrogen and freed from ether in a vacuum desiccator over phosphorus pentoxide. The salt was light pink in color at first and of a yellow color after twenty-four hours. It was distinctly crystalline in character. A yield of 20 g. was obtained.

Anal. Calcd. for C_8H_6NNa: Na, 16.55. Found: Na, 16.57.

The sodium salt is very soluble in the parent nitrile, somewhat soluble in benzene, toluene and xylene and slightly soluble in ether. The reaction mixture contains ether, toluene and unchanged nitrile. The salt is thus quite soluble in the reaction mixture and separates slowly and incompletely. A large excess of ether is desirable since it dilutes the unchanged nitrile and toluene. Cooling increases the rate of precipitation. A second precipitation of the salt usually occurs on long standing of the filtrate.

Identification of Toluene in the Reaction Mixture.—The combined filtrates from five reaction runs, involving a total of 200 cc. of phenylacetonitrile and 1400 cc. of ether, were filtered from precipitated salt and subjected to fractional distillation; 1200 cc. of ether was recovered in the first fraction. The remainder was distilled with an efficient fractionating column. The fraction 110–115°, 54 cc., was again refractionated, yielding

47 cc. boiling at 110–111°, from which there was finally isolated 43 cc. of pure toluene with a boiling point of 110° (corr.). The toluene was further identified by conversion to 2,4-dinitrotoluene; m. p. 70° (corr.).

The higher-boiling fraction yielded a small amount of liquid (unidentified) distilling between 120 and 190°. Between 190 and 240° there was obtained a fraction of 20 cc. consisting chiefly of unchanged phenylacetonitrile. Between 240 and 260° a heavy oil of a red-green color distilled. A small amount of crystalline solid collected in the condenser. These latter were not identified.

Effect of Heat on the Sodium Salt.—The sodium salt obtained from 120 g. of phenylacetonitrile was subjected to rapid heating in a pyrex flask. A small amount of low-boiling liquid was obtained, after which the temperature rose rapidly to 200°. A distillate was obtained of oily appearance and of a green color by reflected light and red by transmitted light. The distillate smelled strongly of ammonia. A considerable amount of crystalline material collected in the condenser tube. This, on recrystallization from alcohol, gave crystals of a wax-like appearance and melting point 123–124°, which is the melting point of stilbene.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.28; H, 6.72. Found: C, 93.41; H, 6.7.

The distillate was treated with an excess of bromine in carbon tetrachloride solution. There appeared almost at once a considerable quantity of fine needle-like crystals. The crystals were removed by filtration and washed well with alcohol. The yield was 4.6 g. The product on recrystallization from hot toluene gave white feathery needles, m. p. 237° (corr.), which is the melting point of stilbene dibromide.

Anal. Calcd. for $C_{14}H_{12}Br_2$: Br, 47.01. Found: Br, 47.11.

The dibromide was converted into tolane by heating with alcoholic alkali. The tolane was precipitated on addition of water, collected and recrystallized from alcohol as white leaflets, m. p. 50–60°. This is the melting point recorded for tolane. These results without doubt identify stilbene as a product of the decomposition of the sodium salt of phenylacetonitrile.

Reactions of the Silver Salt of Phenylacetonitrile.—The silver salt was prepared in an impure form through interaction of the sodium salt and silver nitrate in absolute alcohol solution. There was obtained a white insoluble compound which rapidly became dark in color. This substance decomposes with explosive violence on heating. The silver salt, freshly prepared was mixed with butyl iodide and allowed to stand for twelve hours, after which time a complete reaction had occurred. The mixture possessed a strong odor of isocyanide.

The solution obtained from the reaction mixture of silver salt and butyl iodide was filtered and distilled. The distillate was treated with hydrochloric acid and evaporated to dryness, giving a considerable quantity of white crystalline material. This was purified by recrystallization first from absolute alcohol and then an alcohol–benzene mixture. The substance was butylammonium chloride.

Anal. Calcd. for $C_4H_{12}NCl$: Cl, 32.36. Found: Cl, 32.47.

Condensation of the Sodium Salt of Phenylacetonitrile with Benzalacetophenone.—This condensation was carried out in order to prove that sodium phenylacetonitrile gives the same product that is obtained from phenylacetonitrile using sodium methylate as the condensing agent.

The sodium salt obtained from 2.2 g. of sodium was cooled to the temperature of ice water in a three-necked flask fitted with a stirring device. To this was added 25 cc. of absolute methyl alcohol and then 20 g. of solid benzalacetophenone. The contents of the flask were stirred constantly for three hours, keeping the temperature at 0°. After standing for thirty-six hours there had formed a dense crust of white crystals on the walls of the flask. This was removed, powdered in a mortar and washed with dilute hydrochloric acid to remove sodium compounds, and then with alcohol. There was obtained 24 g. or 93.7% of the theoretical yield of 1,5-dibenzoyl-2,3,4-triphenyl-3-cyanopentane. After recrystallization from chloroform and benzene there was obtained 9.9 g. of pure substance, m. p. 264.5–265.5° (corr.). The substance agrees in every respect with that obtained by Avery.[8]

Anal. Calcd. for $C_{38}H_{31}O_2N$: C, 85.6; H, 6.1; N, 2.6. Found: C, 85.6; H, 5.9; N, 2.5.

This compound has been prepared by Kohler and Allen,[9] who suggest the same structure but who found a melting point of 257". Avery has shown that this melting point is probably low, due to impurities, and that the corrected melting point is 264.5–265.5°.

Summary

1. A method for the preparation of pure sodium phenylacetonitrile is described.
2. New evidence for the existence of tautomeric forms of the nitrile and for the imide structure of the salt is presented.
3. It has been shown that the sodium salt enters into condensation reactions of the type produced by sodium methylate and phenylacetonitrile.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF DIETHYL LEAD DICHLORIDE AND TRIETHYL LEAD CHLORIDE

BY HENRY GILMAN AND JACK D. ROBINSON

RECEIVED DECEMBER 9, 1929 PUBLISHED MAY 8, 1930

Introduction

Convenient methods have been determined for the ready preparation of diethyl lead dichloride and of triethyl lead chloride in essentially quantitative yields by means of the following reactions carried out in toluene and ether, respectively

$$(C_2H_5)_4Pb + 2HCl \longrightarrow (C_2H_5)_2PbCl_2 \qquad \text{(I)}$$
$$(C_2H_5)_4Pb + HCl \longrightarrow (C_2H_5)_3PbCl \qquad \text{(II)}$$

The most generally used method for the synthesis of diethyl lead dihalides is that elaborated by Grüttner and Krause,[1] and involves the direct action of halogens on tetraethyl lead at low temperatures. In that method they recommend that the triethyl lead halide be first prepared at −60° and then converted to the dihalide as the solution warms

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[8] S. Avery, results soon to be published.

[9] Kohler and Allen, THIS JOURNAL, 46, 1522 (1924).

[1] (a) Grüttner and Krause, ***Ber.***, 49, 1415 (1916). (b) Other methods, not of preparative value, for the synthesis of diethyl lead dichloride may be found in the following references: Grüttner, ibid., 47, 3257 (1914); Moller and Pfeiffer, ibid., 49, 2441 (1916); Goddard and Goddard, J. Chem. *Soc.*, 121,256,482 (1922).

up to −20°. When the reaction with halogens is effected at −20° in large-sized runs, without the preliminary formation of triethyl lead halide, they caution against a vigorous reaction which may be of explosive violence. Incidentally, we have shown in this study that it is possible to prepare diethyl lead dichloride in a 98.6% yield by the direct action of chlorine on 0.05 mole of tetraethyl lead in ether cooled to −10°.

The same authors[1"] object to any method for the preparation of triethyl lead chloride which involves the use of hydrogen chloride or hydrochloric acid, basing such objection on the ground that the yield is lowered when large quantities of materials are used. This objection is not valid at least in a preparation starting with 113 g. (0.35 mole) of tetraethyl lead, inasmuch as our yield by Reaction II of triethyl lead chloride is 96%. Triethyl lead chloride has been prepared by Buckton[2] and Cahours[3] by warming tetraethyl lead with concd. hydrochloric acid, and by Buckton[4] from hydrogen chloride and tetraethyl lead. More recently, Browne and Reid[5] have given splendid directions for the preparation of triethyl lead chloride in 86% yields from tetraethyl lead and concd. hydrochloric acid with a trace of silica gel as a catalyst.

The greater stability of the diethyl and triethyl lead chlorides over the corresponding bromides and iodides, as well as their lesser expensiveness, makes them the most desirable halides. This is particularly the case in our studies of their reactions with other organometallic compounds, in which studies they have been shown to have a very high order of reactivity. When, however, it is desired to use the bromide or iodide, then two general methods are available for the conversion of the chloride to the other halides. One involves the hydrolysis to the corresponding hydroxide and subsequent treatment with the appropriate halogen acid.[6] The other method is based on a double decomposition reaction between an alkyl lead halide and the appropriate halide of sodium or potassium.[7] Both of these methods are applicable to the dialkyl lead dihalides as well as to the trialkyl lead halides.

Although we have not tried our method with halogen acids other than hydrochloric acid, it is probable that they can be extended to some of the other halogen acids. Also, it is altogether reasonable to believe that our methods for the synthesis of diethyl lead dichloride and triethyl lead

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[2] Buckton, *Ann.*, 109, 218 (1859).

[3] Cahours, *ibid.*, **122**, 48 (1862).

[4] Buckton, *ibid.*, 112, 220 (1859). See also Pfeiffer and Truskier, *Ber.*, 37, 1125 (1904), who used the same method and reported a good yield, but gave no details as to solvent, percentages, purity, etc.

[5] Browne and Reid, THIS JOURNAL, 49, 830 (1927).

[6] Krause and Pohland, *Ber.*, 55, 1282 (1922).

[7] Löwig, *J. prakt. Chem.*, 60, 304 (1853); Klippel, *ibid.*, 81, 287 (1860); and References 2 and 3 of this paper.

chloride are applicable to tetra-alkyl lead compounds other than tetraethyl lead.

Experimental Part

Diethyl Lead Dichloride, $(C_2H_5)_2PbCl_2$.—After dissolving 107.5 g. (0.3 mole) of tetraethyl lead in 500 cc. of toluene in an open[8] Erlenmeyer flask, and heating the solution to 90°,[9] dry hydrogen chloride is passed into the solution at a moderate rate. Inasmuch as the triethyl lead chloride which first forms is soluble in toluene, no precipitate appears before one-half of the hydrogen chloride has been absorbed. The approximate end of the reaction may be determined by adding hydrogen chloride at the same rate for twice the time necessary to cause the first precipitate of diethyl lead dichloride to form. At this stage the precipitate is removed by filtration and hydrogen chloride is again added in order to precipitate any unreacted triethyl lead chloride. If no precipitate forms on this subsequent addition of hydrogen chloride, the reaction is ended. The yield of 107 g. or 97.5% has been checked many times. The product is free of lead chloride, and if there were any significant quantity of triethyl lead chloride it would probably not contaminate the diethyl lead dichloride because of its high solubility in hot toluene.[10]

In another connection, chlorine was bubbled slowly into a well-stirred solution of 16.5 g. (0.05 mole) of tetraethyl lead dissolved in 150 cc. of dry ether and cooled to −10°. A smooth reaction occurred, and when the chlorine colored the solution, the reaction was considered to be complete. The diethyl lead dichloride was filtered off, and its weight was 16.6 g. which is equivalent to a 98.6% yield. This describes the only experiment we carried out between tetraethyl lead and chlorine.

Triethyl Lead Chloride, $(C_2H_5)_3PbCl$.—Forty-eight and one-half grams (0.15 mole) of tetraethyl lead is dissolved in 400 cc. of absolute ether and saturated with hydrogen chloride at room temperature. This requires about thirty minutes or more. depending on the rate of flow of gas. The rate at which the hydrogen chloride is absorbed appears to reach a maximum and the evolution of ethane is rather constant. Perhaps the best way to determine when the reaction is at an end is to remove the needles of triethyl lead chloride by filtration when the ethane is only slowly evolved, and then to saturate the filtrate again with hydrogen chloride. If no more needles form, the reaction is complete. The yield is 48.6 g. or 98.2%.[11]

In this preparation it is necessary that all moisture be rigorously excluded from the flask and reagents. Triethyl lead chloride is soluble in moist ether but quite insoluble in dry ether which contains moderate amounts of hydrogen chloride. However, triethyl lead chloride appears to be appreciably soluble in dry ether which contains a *large* quantity of hydrogen chloride. This finds support in two observations. First, it has been found that on boiling a solution to remove excess hydrogen chloride, another

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[8] All operations are carried out, of course, with due care because of the toxicity of tetraethyl lead. This involves, primarily, working in a well-ventilated hood. Care should be exercised about long exposure to triethyl lead chloride. The observation of Krause and Pohland, *Ber.*, 55, 1282 (1922), that compounds of this type cause severe headaches has been confirmed.

[9] The temperature of the solution should be maintained at 90° by the application of heat, although there appears to be no harm with a temperature variation of 10°.

[10] The diethyl lead dichloride is in the reactive form and requires no further treatment prior to use. See Griittner and Krause, *Ber.*, **49**, 1546 (1916).

[11] The yields may vary between 92 and 98.2% depending on the careful conversion of the last small quantities of tetraethyl lead. The smoothness of these reactions has recommended them for other studies concerned with the lability or polarity of radicals.

crop of crystals frequently appears. Second, the saturation of a suspension of triethyl lead chloride in ether with hydrogen chloride induces some of the triethyl lead chloride to dissolve. This latter phenomenon appears to be unusual with organolead halides.

Summary

Diethyl lead dichloride and triethyl lead chloride can be very conveniently prepared in essentially quantitative yields by the reaction between tetraethyl lead and hydrogen chloride.

AMES, IOWA

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

SOME PHYSICAL CONSTANTS OF MONACETIN, MONOPROPIN AND MONO-NORMAL-BUTYRIN[1]

BY H. A. SCHUETTE AND JOHN T. HALE

RECEIVED DECEMBER 12, 1929 PUBLISHED MAY 8, 1930

The discovery of the nature of fatty oils by Chevreul over a century ago gave a marked impetus to the synthesis of simple and mixed glycerides. The monoglyceryl esters of the acids of low molecular weight have not, however, shared the same degree of interest. Published information thereon is apparently non-existent for one of the esters pertinent to this communication; the reported physical constants of another are obviously in need of correction; and such data as are available have been determined at temperatures for which there is no uniformity.

In view of this situation there is an evident need for new data and for a revision of some of that now extant. These ends have been accomplished by the synthesis of the glycerides in question and the determination of their vapor pressures, densities, refractive indices and surface tensions. The method of preparation which was followed led to the formation of racemic compounds which probably possess, as might be expected, different constants than the corresponding naturally occurring glycerides, none of which, however, seems to have been isolated.

Monacetin has been made by Berthelot,[2] who heated a mixture of glycerol and acetic acid under pressure; by Geitel,[3] who isolated it from the reaction product resulting from heating a mixture of glycerol and acetic acid at atmbspheric pressure; by Averill, Roche and King,[4] who synthesized a-monoglycerin by a method developed by Fischer[5] and his

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[1] Constructed from a thesis submitted by John T. Hale to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Master of Science, June, 1928.

[2] Berthelot, *Ann. chim. phys.*, [3] 41, 216 (1854).

[3] Geitel, *J. prakt. Chem.*, 163, 417 (1897).

[4] Averill, Roche and King, THIS JOURNAL, 51, 866 (1929).

[5] Fischer, Bergwin and Barwind, *Ber.*, 53, 1589 (1920).

collaborators; and by one of us,[6] who improved upon Geitel's technique by introducing a suitable catalyst into the reaction mixture. Butyrin was made by Berthelot by a method already indicated;[2] by Guth[7] from sodium butyrate and α-monochlorohydrin; and by Hanriot, it is reported,[8] who used a biological method of synthesis in that he caused lipase to act upon a mixture of glycerol and butyric acid.

Experimental

A uniform method of procedure was followed in the synthesis of the monoglycerides pertinent to this communication. Its salient features consist of the use of phosphoric acid as catalyst; an esterification temperature whose order of magnitude is lower than that of the boiling point of the acid in question; and the removal of by-product water as fast as it is formed. The last two conditions were met by dispersing the reactants in carbon tetrachloride and carrying out the operation with the aid of a continuous separator.[9]

Because of the similarity in method the synthesis of but one glyceride is described as illustrative of a typical case. In each instance equivalent quantities of glycerol and fatty acid necessary to produce the monoglyceride in question were taken.

That a monoglyceride had actually been synthesized was deduced from the satisfactory degree of agreement between the molecular refractivity (Gladstone and Dale formula) and the sum of the atomic refractivities of the compound in question. Although it is true that no claim for great delicacy can be made for this method of identification, yet it would seem that, in this instance, the assumption is valid in view of the close concordance between observed and theoretical saponification equivalents.

Monopropin.—A mixture consisting of 150 g. of glycerol (1 mol), 118 g. of propionic acid (1 mol) (b. p. 140–141°), 10 g. of phosphoric acid (85%) and 200 cc. of carbon tetrachloride was heated under a reflux for approximately four hours, during which time an amount of water was recovered which was slightly in excess of the theoretical. Ten g. of sodium propionate was then added to the reaction mixture, and the whole concentrated by distillation at a temperature below 130°. The insoluble phosphate was then removed by filtration, whereupon the filtrate was distilled at a pressure of 3 mm., the fraction boiling between 132–134°, indicative of a 58% yield, being saved for further purification.

The following constants were noted: d_4^{20} 1.1537, n_{20} 1.4503; saponification equivalent, 148.2, calcd. for monopropin, 148.1; molecular refraction, 57.81, calcd. for monopropin, 57.18; γ_{20} 40.3 dynes/cm.

Monacetin.—The fraction boiling between 129–131° (3 mm.) on purification yielded the following constants: d_4^{20}, 1.2060; n_{20} 1.4517; saponification equivalent, 134.1,

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[6] Schuette and Sah, THIS JOURNAL, 48, 3161 (1926).

[7] Guth, *Z. Biol.*, 44, 78 (1903).

[8] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," Macmillan Co., London, 1921, 6th ed., Vol. I, p. 8.

[9] Hultman, Davis and Clarke, THIS JOURNAL, 40, 366 (1921).

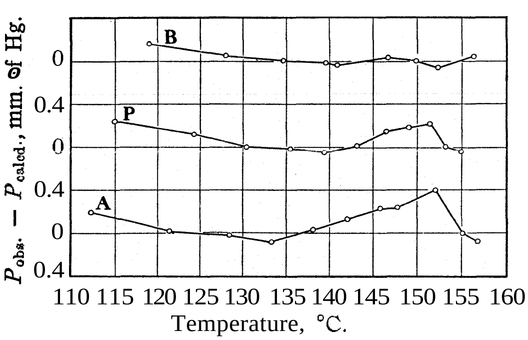
calcd. for monacetin, 134.2; molecular refraction, 50.21, calcd. for monacetin, 49.53; γ_{20} 47.1 dynes/cm.; yield of crude ester, 70%.

Mono-*n*-butyrin.—The fraction boiling between 139–140° (4 mm.) on purification yielded the following constants: d_4^{20} 1.1344; n_{20} 1.4531; saponification equivalent, 162.1, calcd. for monobutyrin, 162.1; molecular refraction, 64.75, calcd. for monobutyrin 64.83; γ_{20}, 37.6 dynes/cm.; yield of crude ester, 78%.

Vapor Pressure Measurements

Measurements of the vapor pressure of the three glycerides were made by the method of Ramsay and Young[10] over a temperature range of approximately 120°, minimum and maximum being 112 and 238°, respectively. Inasmuch as decomposition probably occurred in the upper zones, the values there observed have not been recorded. Temperatures were read with a thermometer graduated to 0.2°. They were corrected for stem exposure. Pressures were read to 0.1 mm. on an ascending and a descending temperature scale. When these data were subsequently plotted it was found that the observed points fell on one curve.

The curve for the vapor pressure of monacetin may be expressed by the empirical equation log P = 10.10518 − 3864.8/T. It holds for temperatures up to approximately 185°, and is reliable down to 112°. Similarly the equation for monopropin was found to be 10.29682 − 3961.3/T, an expression which is valid between the temperatures 115 and 183°. For mono-n-butyrin the curve for the vapor pressure corresponds to the equation log P = 10.78092 − 4200.8/T. It holds between the limits 119 and 176".



A, monacetin; P, monopropin; B, mono-n-butyrin.

Fig. 1.—Deviation plot.

Though due recognition is made of the fact that equations of this character are at best but approximate, yet the fact remains that the experimental points were found to lie on straight lines within the limits of accuracy of the experimental data. The least accurate factor probably lies in whatever limitations are inherent in the method which was employed for determining the vapor pressures.

That the differences between the experimentally determined and calculated vapor pressures might be graphically shown, there is reproduced a deviation plot (Fig. 1) for each of the glycerides pertinent to this study. Maximum and mean differences were found to be 0.40 and 0.12 mm.

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[10] Ramsay and Young, J. Chem. *Soc.*, **47,** 42 (1885).

for monacetin. Similarly for monopropin and mono-n-butyrin these differences are 0.24 and 0.09, and 0.16 and 0.04, respectively.

Conclusions

The foregoing expressions of the vapor pressure–temperature relationships which obtain among the monoglycerides of low molecular weight make possible a critical inspection of such boiling points of these compounds as have found their way into some of the well-known texts and reference books. When viewed in the light of the data as herein recorded, it appears that the previously reported boiling points of monacetin of 189–191 (60 mm.)[6] and 130–132° (2–3 mm.)[8] are in substantial agreement with our observations. On the other hand, the statement[11] that monacetin boils at 158° (165 mm.) is rather difficult to explain except perhaps on the grounds of a typographical error in recording the pressure.

That monobutyrin boils at 269–271°[8] or at 271°[11] under atmospheric pressure appears to be an absurd statement because of the generally accepted view that the glycerides cannot be distilled under ordinary conditions without decomposition, and the fact that the calculated boiling point of this glyceride is approximately 535°. The assigned boiling point of 160–163° (16 mm.)[8] is in better agreement with fact.

The heat of vaporization per gram of ester when calculated with the aid of the Clausius–Clapeyron equation is for monacetin 132.4 cal., for monopropin 122.5 cal. and for mono-n-butyrin 118.75 cal.

Summary

The monoglycerides of acetic, propionic and n-butyric acids have been synthesized and their simpler physical constants determined at a uniform temperature. Of these data those for monopropin are new.

The vapor pressures of these glycerides have been determined over the temperature range in which they are stable.

The heats of vaporization have been calculated.

MADISON, WISCONSIN

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[11] National Research Council, "International Critical Tables," McGraw-Hill Book Company, Inc., New York, 1926, Vol. I, p. 193.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

AN INVESTIGATION OF A SERIES OF DERIVATIVES OF NORMAL HEPTANE. I. PREPARATION, IDENTIFICATION AND PHYSICAL CONSTANTS

BY MARY L. SHERRILL[1]

RECEIVED DECEMBER 14, 1929 PUBLISHED MAY 8, 1930

In connection with further investigation of isomeric hydrocarbons similar to those obtained in the case of 2-pentene[2] it was found necessary to prepare and identify certain derivatives of normal heptane. The preparation, purification and identification of these products and the physical constants measured furnish the basis for the present paper. The measurement of the dielectric constants and the determination of the dipole moments of these compounds are given in the following paper. The work involved a study of the four straight-chain alcohols, heptanol-1, heptanol-2, heptanol-3, heptanol-4, the corresponding chloro and bromo derivatives, two of the iodo derivatives, and the aldehyde and the ketones obtained from these alcohols.

Experimental

Determination of Physical Properties

Boiling Point.—All distillations were made at diminished pressure except in a few specified cases. A fractionating column (a modified Vigreux type) 50 cm. in length, was used for these distillations. The receiver was so arranged that fractions could be removed and new receivers put on (evacuated by an auxiliary pump) so that the distillation could be continuous. In the case of distillations at atmospheric pressure the fractionating column was 50 cm. long, of the Crismer type, consisting of a glass spiral fitting closely around an inner tube, the tube and spiral fitting snugly into the column. The thermometers used were of the Anschiitz type, calibrated by the Physikalisch-Technische Reichsanstalt, and were placed in the side neck so that the mercury was completely immersed in vapor.

Freezing Point.—The freezing point determinations were made by Professor Jean Timmermans.[3] Approximately 5-cc. samples, in 15–18-cm.

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[1] C. R. B. Fellow, University of Brussels, 1928–1929. The experimental work included in this and the following paper was done at the University of Brussels. The writer wishes to express appreciation to the C. R. B. Educational Foundation for the opportunity given for study and also to acknowledge a very generous grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences which made possible the investigation.

[2] Sherrill, Otto and Pickett, THIS JOURNAL, 51, 3027–3033 (1929); Sherrill, Haas and Baldwin, *ibid.*, 51, 3034–3041 (1929); Carr, *ibid.*, 51, 3041–3053 (1929).

[3] The author takes this opportunity of expressing appreciation of Professor Timmermans' interest and cooperation.

test-tubes, were cooled in liquid air and the temperature of the freezing point measured by Professor Timmermans' specially calibrated thermometers.

Density.—The density determinations were made in a 14-cc. Sprengel pycnometer and at least three checking determinations were made at each temperature. The measurements at 0° were made by surrounding the pycnometer with finely crushed ice, those at 15° were made in a Dewar flask in which the temperature remained constant within less than 0.1° over several hours, those made at 20° were made in a thermostat regulated constant to at least 0.01°. The weights were reduced to a vacuum basis.

Index of Refraction.—The refractive indices for the three helium lines, at 15 and 20° or at 17.5 and 20° were measured with a Pulfrich refractometer, supplied with a calibrated thermometer graduated in tenths of degrees. The water current through the refractometer came from an accurately regulated thermostat. The temperatures were accurate within 0.05'. Duplicate observations checked closely. The refractive indices for the sodium D line were made with an Abbé refractometer. The water current through the refractometer came from a thermostat.

Following each table of physical data there is a summary of literature data, complete in the case of the halogen derivatives, representative in the case of the other compounds.

Purification of **Heptanols.**—Three of the heptanols which were the source materials for the work were prepared especially for this problem by R. E. Marker by means of the Grignard synthesis from the corresponding alkyl bromide and alkyl aldehyde. These alcohols were methyl-*n*-amyl carbinol, ethyl-n-butyl carbinol and dipropyl carbinol. The fourth alcohol, n-heptanol, was obtained from Schering-Kahlbaum. In each case the alcohols were carefully dried and fractionated in *vacuo* in order to diminish any possibility of dehydration which might give a mixture of hydrocarbon and alcohol. Three distillations were made although the alcohols boiled very constantly in the second distillation. The boiling points and indices of the distillates in the second and third distillations were the same. The identity of the alcohols was proved by the oxidation of each and the preparation of the corresponding semicarbazone. In each

TABLE I

CONSTANTS OF HEPTANOLS

	Alc. fract., g.	Const. b. prod. (final dist.), g.	°C. ± 0.1°	Boiling points			$\frac{dt}{dp}$	Mm.
				mm.	°C. ± 0.05°	mm.		
Heptanol-1	535	428	175.9	759.5	84.7	20	0.6°	20–22
Heptanol-2	1100	480	158.7	740.5	66.7	16.5	.4°	16–18
Heptanol-3	963	536	155.9	740.5	65.8	20	.4°	16–20
Heptanol-4	605	184	155.4	755.2	63.8	16	.45°	16–20

TABLE I (*Concluded*)

	F. p., °C.	Density, t°/4° 0°	15°	20°	M. p. of semicarbazone from ox. of alc., °C.
Heptanol-1	.....	0.8359[a]	0.8260	0.8227	109
Heptanol-2	Vitreous	.8315	.8203	.8167	123
Heptanol-3	Vitreous	.8370	.8251	.8210	88
Heptanol-4	−41.5	.8335	.8219	.8183	132

[a] Pycnometer used had a capacity of 6 cc.

Indices of refraction of the heptanols

	Helium red 15°	Helium red 20°	Helium yellow 15°	Helium yellow 20°	D 20°	Helium green 15°	Helium green 20°
Heptanol-1	1.42351	1.42190	1.42627	1.42456	1.4245	1.43043	1.42874
Heptanol-2	1.42059	1.41857	1.42336	1.42125	1.4210	1.42755	1.42527
Heptanol-3	1.42169	1.41967	1.42436	1.42236	1.4222	1.42845	1.42636
Heptanol-4	1.41987	1.41806	1.42256	1.42065	1.4205	1.42665	1.42467

case the semicarbazone without purification gave a sharp melting point which checked the most recent literature data.[4,5]

Literature Data

Heptanol-1.—B. p. (760 mm.) 175.8–176.2°, d_4^{25} 0.8187, n_D^{25} 1.4224;[6] b. p. (751.2 mm.) 174.4°, $d_4^{34.6}$ 0.8116;[7] b. p. (755 mm.) 175.5°, d_4^{22} 0.8173; d_4^{32} 0.8106;[8] b. p. (12 mm.) 76°;[9] d_4^{20} 0.8237;[10] b. p. 172.5–173°, $d_4^{22\ 4}$ 0.8206, $n_\alpha^{22.4}$ 1.42116, n_D 1.42326, $n_\beta^{22\ 4}$ 1.42843, $n_\gamma^{22\ 4}$ 1.43281, $d_4^{24\ 4}$ 0.8190, $n_\alpha^{24\ 4}$ 1.42043, $n_D^{24\ 4}$ 1.42242, $n_\beta^{24\ 4}$ 1.42770, $n_\gamma^{24\ 4}$, 1.43196.[11]

Heptanol-2.—(a) Inactive, b. p. (762 mm.) 156–157°, d_{20} 0.8193, n_D 1.42131;[12] b. p. 157–158°, d^0 0.8344;[13] b. p. 158–160°;[14]—(b) dextro: b. p. (20 mm.) 73.5°, d_4^{20} 0.8190, n_D^{20} 1.4209;[14]—(c) levo: b. p. (23 mm.) 74.5°, d_4^{20} 0.8184.[14]

Heptanol-3.—(a) Inactive: b. p. (750 mm.) 156.5–157°;[15] b. p. 150–152°;[14] b. p. (745 mm.) 152.7–154°, d_4^{25} 0.8159, n_D^{20} 1.4201, n_D^{25} 1.4175;[16]—(b) dextro: b. p. (18 mm.) 66°, d_0^{13} 0.8248, d_0^{50} 0.7985, d_4^{20} 0.8227.[14]

Heptanol-4.—B. p. 153–154°, d_4^{15} 0.822, n_D^{15} 1.4226;[9] b. p. (767 mm.) 154.5°,

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[4] Mathus and Gibon, *Bull. soc. chim. Belg.*, 34,303 (1925).

[5] Harries and Oppenheim, *Chem. Zentr.*, 11,992 (1916); *C. A.*, 11,3237 (1917).

[6] Norris and Cortese, THIS JOURNAL, 49,2644 (1927).

[7] Verkade and Coops, *Rec. trav. chim.*, 43, 903–917 (1927); see Ref. 8.

[8] Carrara and Ferrari, *Gazz. chim. ital.*, 36, I, 424 (1906); summary of data: "Revues Critiques de Constantes Fascicule VI," Union Internationale de la Chemie pure et appliquée par le Bureau International des Étalons Physico-Chimiques Université de Bruxelles, edited by Jean Timmermans, p. 57 (1928).

[9] Vavon, *Ann. chim.*, [9] 1, 176 (1914).

[10] Lowry, *J. Chem. Soc.*, **105**, 92 (1914).

[11] Eisenlohr, *Z. physik. Chem.*, 75, 588 (1911).

[12] Henry and de Wael, *Rec. trav. chim.*, 28, 446 (1909); *Chem. Zentr.*, I, 1854 (1909).

[13] Masson, *Compt. rend.*, 149, 630 (1909).

[14] Pickard and Kenyon, *J. Chem. Soc.*, 99, 57, 58, 65 (1911); 101, 638 (1912); 103,1936, 1943, 1957 (1913); 105,849 (1914).

[15] Blaise and Picard, *Compt. rend.*, 152, 446 (1911); *Ann. chim.*, [8] 26,286 (1912).

[16] Dillon and Lucas, THIS JOURNAL, 50, 1711 (1928).

d_4^{20} 0.8183, n_D^{20} 1.4205;[17] b. p. (750 mm.) 155.00 ± 0.04°, d_4^{25} 0.8129, n_D^{25} 1.4178;[18] b. p. (760 mm.) 155.9–156°, d_4^{25} 0.8156, n_D^{25} 1.4184;[6] b. p. (745 mm.) 153.4–154.3°, m. p. −41.5" to −37.2°, d_4^{25} 0.8175; n_D^{20} 1.4199, n_D^{25} 1.4173.[16]

Halogen Derivatives—Each of the four chlorides and four bromides was prepared; the 3-iodoheptane was prepared; and the 1-iodoheptane (Schering–Kahlbaum) was purified. Especial care was taken in the preparation to prevent a shift of the position of the entering halogen and for the same reason the distillation was carried out under diminished pressure. The products were of very constant boiling point, showing no change on second distillation, and in each case, except for very small cuts at the beginning and the end, the distillate boiled completely within one-tenth of a degree.

The chloro derivatives were prepared by the action of concentrated hydrochloric acid and zinc chloride on the heptanols according to an adaptation of the method of Norris and Taylor.[19] One mole of the heptanol was added to two moles of ice-cold concentrated hydrochloric acid containing two moles of anhydrous zinc chloride. The product was kept in an ice-bath for several hours and vigorously stirred. Then the mixture was gradually allowed to come to room temperature. In the case of 1-chloroheptane the reaction mixture was refluxed gently for one hour and then the oil was slowly distilled off. With the 2-, 3- and 4-chloro derivatives the method was varied as suggested by Lucas,[20] the reaction being carried out at a lower temperature in order to avoid as much as possible any shift of position in the chain. The mixture of heptanol, hydrochloric acid and zinc chloride was kept ice cold for six to eight hours; then it was allowed to come to room temperature. After the mixture had stood from twelve to twenty-four hours, the oil layer was removed and the process repeated. The oil was added to fresh portions of ice-cold concentrated hydrochloric acid (two moles) and zinc chloride (two moles). This was repeated at the end of a second twenty-four hour period. Finally the oil and acid mixture was vigorously shaken.

For purification the chloride layer was separated from the water–acid layer, was washed three times with fresh portions of concentrated hydrochloric acid, four times with ice-cold water, once with 10% sodium hydroxide (ice cold) and twice with cold 15% sodium chloride. The crude oils, very pale yellow in color, were dried over calcium chloride and distilled twice *in vacuo* over phosphorus pentoxide. The crude yields were 77–80% of the theoretical and the yields of constant boiling products were from 60–64% of the theoretical yields. The purified chloro derivatives were perfectly colorless and have remained so for six months.

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[17] Krapiwin, Chem. Zentr., I, 1335 (1910).

[18] Brunel, THIS JOURNAL, 45, 1334 (1923).

[19] Norris and Taylor, *ibid.*, 46, 753–757 (1924).

[20] Lucas, *ibid.*, 51, 249 (1929).

The 1-bromo derivative was prepared according to methods used for similar bromides by Kamm and Marvel,[21] Norris, Watt and Thomas[21] and Simon.[22] Eighty-eight grams of 1-heptanol was refluxed for two and one-half hours with 360 g. of 48% hydrobromic acid to which 92 g. of concentrated sulfuric acid had been added. The oil was separated and washed with water but proved to be lighter than water, so the procedure was repeated and the material was refluxed for three hours. The oil, when separated and washed with concentrated sulfuric acid, with water and with sodium carbonate, was so dark in color that it was distilled from four times its volume of 48% hydrobromic acid, which gave a practically colorless product.

The 2-, 3- and 4-bromo derivatives were prepared by slow saturation of the alcohols with hydrogen bromide.[2] The heptanol was kept at a temperature of about −10° by an ice and salt bath and a slow stream of hydrogen bromide was passed into the alcohol during a period of six to eight hours. The flask was then closed with a capillary tube or a tube carrying a rubber balloon and the mixture was allowed to come to room temperature and left overnight. The process was repeated each day for twelve days.

The bromides were purified as in the case of the chlorides by washing with 48% hydrobromic acid, water and sodium hydroxide and were dried over anhydrous calcium chloride. Then each was distilled twice in *vacuo* over phosphorus pentoxide. The crude yields of bromide were 70% of the theoretical in the case of 1-bromo-, and 85–90% in the case of the other three derivatives. The yields of constant boiling products were from 65–75% of the theoretical. The bromoheptanes so obtained showed no trace of color and have remained colorless for six months.

The 1-iodoheptane was obtained from Schering–Kahlbaum. It was shaken with mercury to remove excess iodine, filtered and distilled in *vacuo.* Eighty per cent. of the distillate was a constant boiling product and the iodoheptane so obtained has remained almost colorless for six months.

The 3-iodoheptane was prepared by a method analogous to that used for the preparation of the chloro derivatives. One hundred and thirty grams of 3-heptanol was treated with 750 g. of hydriodic acid in three separate portions and the mixture left for sixty hours, being agitated frequently. At the end of that time the oily layer was washed and found to be lighter than water so it was put back with the hydriodic acid and zinc iodide and refluxed for two hours at 60–70°. The reaction was still incomplete so gaseous hydrogen iodide was passed into the oily mixture of 3-iodoheptane and 3-heptanol for about five hours. At the end of this time

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[21] **Kamm** and Marvel, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1921,** Vol. I, p. 7; Norris, Watt and Thomas, THIS JOURNAL, 38, 1075 (1916).

[22] Simon, Bull. *soc. chim. Belg.*, 38, 48 (1929).

100 g. of the hydriodic acid (sp. gr. 1.5) and 100 g. of zinc iodide were added and the mixture left for twenty-four hours. The oil was then separated, purified as in the case of the chloro and bromo derivatives and distilled in *vacuo*. The distillation showed that the reaction was not complete, for there were two distinct distillates, one boiling fairly constantly at 75.2–75.6' at 30 mm. for more than an hour; then there was an interval (twenty-five minutes) when there was practically no distillate. Then the temperature rose rapidly to 88.8' at 30 mm. and a second constant boiling product distilled. This product was about 50% of the distillate.

Proof of Position of **the** Halogen.—In order to test the position of the substituting halogen each of the chloro derivatives was treated in the following manner. Approximately 10 g. of the chloro derivative was refluxed for seven hours with 15 g. of anhydrous potassium acetate and 10 g. of glacial acetic acid. The product was diluted with water and the ester extracted with ether. The ether was then removed by distillation and the ester was hydrolyzed by refluxing for six hours with 50 cc. of alcoholic potash (20% solution). The larger part of the ethyl alcohol was removed by distilling up to 85° (some of the heptanol distilled also, as was evidenced by the odor). Water was then added to the residue and an ether extraction was made. The ether was distilled off and the distillation continued up to 90° to remove all traces of ethyl alcohol. The residue of heptanol (approximately 3 g.) was oxidized by acidified bichromate. A solution of bichromate (2.7 g. in 35 cc. of water) was divided into two portions. Half was added to the heptanol; to the other half, 2.2 cc. of concd. sulfuric acid was added and this acid mixture was poured, drop by drop, into the well cooled mixture of heptanol and bichromate. The entire mixture was refluxed at 70–80° for one hour and a quarter. About 100 cc. of water was then added and the mixture distilled as long as oil distilled over. The ketone (or aldehyde) was separated from the water layer and washed several times with sodium carbonate solution. The ketone (approximately 2 g.) was then transformed into the semicarbazone by treatment with semicarbazide hydrochloride and sodium acetate. The semicarbazones formed were in each case similar in crystal form to those obtained from the original alcohols and they gave, without purification, the same melting points. The semicarbazone from 4-chloroheptane melted slightly lower, 129–130° and less sharply than the one obtained from the original, 132°. Mixed melting points with the original semicarbazones showed no change.

The 2-, 3- and 4-bromo derivatives were esterified, hydrolyzed and oxidized as in the case of the chloro derivatives, and the semicarbazones formed from the ketones were identical with those from the corresponding alcohols, except in the case of the 3-bromo, the semicarbazone from which melted at 96–97'. The amount of ketone obtained was small and the semicarbazone was filtered after standing for several days. The amount obtained was too small for purification. A mixed melting point of equal portions of this semicarbazone and of the pure semicarbazone, m. p. 88–89', melted at 90–91°, which indicated that it was the semicarbazone of 3-heptanone with some impurity. There are two points of interest to be noted in connection with this: first that Pickard and Kenyon[14] and Michael[23] give values 99–100° and 103° for the melting point of this substance, Mathus and Gibon[4] giving the lower value 89°. Second, in the preparation of the semicarbazone from 3-heptanol a large yield (12 g.) crystallized out instantly and melted at 88–89' sharply. A second precipitate (less than 2 g.) which came out after several days of standing melted at 97–98'. This material mixed with the 88–89' product melted at 90–91°. This seems to indicate that on oxidation of 3-heptanol, in addition to the 3-heptanone, there is a small amount of another ketone or other impurity which on long standing gives a semicarbazone.

TABLE II

CONSTANTS OF THE CHLOROHEPTANES

	Chloro der. fract., (vac.) g.	Const. b. prod. (final dist.), g.	Boiling points °C. ± 0.05°	Boiling points Mm.	$\frac{dL}{dp}$	Mm.
1-Chloroheptane	170	138	61.4	27	0 5°	25–27
2-Chloroheptane	65	59	46.0	19.5	.5°	19.2–22.5
3-Chloroheptane	75	61	48.3	21	.4°	21–24
4-Chloroheptane	50	38	48.9	21	.5°	20–22

	F. p.. °C.	Density, $t°/4°$ 0°	Density, $t°/4°$ 15°	Density, $t°/4°$ 20°	M. p. of semicarbazone from chloro deriv., °C.
1-Chloroheptane	−69.5	....	0.8783	0 8725	108.8–109.2
2-Chloroheptane	..	0.8848	.8725	.8672	123
3-Chloroheptane	..	.8866	.8732	.8690	88–89
4-Chloroheptane	..	.8884	.8751	.8710	129

Indices of refraction of the chloroheptanes

	Helium red 15°	Helium red 20°	Helium yellow 15°	Helium yellow 20°	D 20°	Helium green 15°	Helium green 20°
1-Chloroheptane	1.42381"	1.42261	1.42657[a]	1.42537	....	1.43084"	1.42964
2-Chloroheptane	1.42170	1.41967	1.42446	1.42246	1.4221	1.42884	1.42675
3-Chloroheptane	1.42251	1.42068	1.42547	1.42336	1.4228	1.42973	1.42755
4-Chloroheptane	1.42270	1.42078	1.42557	1.42346	1.4231	1.42983	1.42765

[a] Temperature, 17.5°.

Literature Data

1-Chloroheptane.—B. p. (750 mm.) 159.2°, d^{16} 0.881;[24] b. p. 159°.[25]

2-Chloroheptane.—Beilstein records that it is unknown in pure form; b. p. 165–170°.[26]

3-Chloroheptane.—B. p. (751 mm.) 143.4–144.4°, n_D^{20} 1.4237.[16]

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[23] Michael, THIS JOURNAL, 41, 411–424 (1919).

[24] Cross, Ann., 189, 3 (1877).

[25] Sabatier and Mailhe, *Compt.* vend., 169, 124 (1919).

[26] Schorlemmer and Thorpe, Ann., 217,152 (1883).

4-Chloroheptane.—B. p. (751 mm.) 143.1–144.4°, n_D^{20} 1.4237;[16] b. p. (758 mm.) 144–145°, d_4^{20} 0.8619, n_D^{20} 1.4199.[4]

TABLE III

CONSTANTS OF THE BROMOHEPTANES

	Bromo der. fract. (vac.), g.	Const. b. prod. (final dist.), g.	Boiling points °C. ± 0 05°	Boiling points Mm.	$\frac{dt}{dp}$	Mm.
1-Bromoheptane	80	63	70.6	19	0.7°	19–23
2-Bromoheptane	165	136	66.2	24	.6°	24–25
3-Bromoheptane	135	88	62.0	18	.5°	18–20
4-Bromoheptane	50	38	60.0	18	.7°	18–20

	F. p., °C.	Density, t°/4° 0°	Density, t°/4° 15°	Density, t°/4° 20°	M. p. of semicarbazone from bromo deriv., °C.
1-Bromoheptane	—58 25	1.1596	1.1488	1.1384	.....
2-Bromoheptane	...	1.1493	1.1333	1.1277	122–123
3-Bromoheptane	...	1.1577	1.1415	1.1362	96–97
4-Bromoheptane	...	1.1565	1.1404	1.1351	129–130

Indices of refraction of bromoheptanes

	Helium red 15°	Helium red 20°	Helium yellow 15°	Helium yellow 20°	D 20°	Helium green 15°	Helium green 20°
1-Bromoheptane	1.44934	1.44734	1.45260	1.45049	....	1.45765	1.45546
2-Bromoheptane	1.44673	1.44461	1.44999	1.44789	1.4476	1.45506	1.45295
3-Bromoheptane	1.44954	1.44744	1.45290	1.45069	1.4503	1.45785	1.45575
4-Bromoheptane	1.44894	1.44673	1.45210	1.44989	1.4495	1.45716	1.45496

Literature Data

1-Bromoheptane.—B. p. (750.6 mm.) 178.5°, d^{16} 1.133;[24] b. p. (765 mm.) 175.5–177.5°.[27]

2-Bromoheptane.—B. p. 165° with decomposition;[28] b. p. 165–167°, $d^{17.5}$ 1.422 (cf. 1.1422, Beilstein).[29]

3-Bromoheptane.—B. p. (74 mm.) 84.5–85.5°, n_D^{20} 1.4507.[16]

4-Bromoheptane.—B. p. (72–75 mm.) 84.0–85.5°, n_D^{20} 1.4506;[16] b. p. 159–160°, ordinary pressure, b. p. (11 mm.) 55°, d_4^{20} 1.1389, n_D^{20} 1.4472, transformed into mixture by atmospheric distillation.[4]

Bromoheptane (position of bromine uncertain) b. p. (70 mm.) 93°, d_4^0 1.1577.[30]

TABLE IV

CONSTANTS OF IODOHEPTANES

	Distillate g.	Const. b. prod., g.	Boiling pt. °C. ± 0.05°	Boiling pt. Mm.	$\frac{dt}{dp}$	Mm.	Density,[a] t°/4° 15°	Density,[a] t°/4° 20°
1-Iodoheptane	81	65	97.0	26	0.5"	25	1.3870	1.3774
3-Iodoheptane	115	55	88.9	30	..	..	1.3735	1.3676

Indices of refraction of iodoheptanes

	Helium red 17.5°	Helium red 20°	Helium yellow 17.5°	Helium yellow 20°	Helium green 17.5°	Helium green 20°
1-Iodoheptane	1.48760	1.48689	1.49193	1.49107	1.49867	1.49771
3-Iodoheptane	1.48915	1.48812	1.49346	1.49241	1.50037	1.49923

[a] The densities of the iodo derivatives were measured by M. Cambron at the University of Brussels.

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[27] Bogert, THIS JOURNAL, **25**, 289 (1903).

[28] Schorlemmer, *Ann.*, **188**, 253 (1877).

[29] Venable, Ber., 13, 1650 (1880); Wheeler, THIS JOURNAL, **25**, 532 (1903).

[30] Francis and Young, J. *Chem. Soc.*, 73,921 (1898).

Literature Data

1-Iodoheptane.—B. p. (754.8 mm.) 201°, d^{16} 1.346;[24] b. p. (16.5 mm.) 91°;[31] b. p. (20 mm.) 93–95°;[32] 203.8°, ordinary pressure, d_0^0 1.4008.[33]

3-Iodoheptane.—B. p. (8.5 mm.) 64.5°.[15]

Aldehyde and Ketone Derivatives.—The *n*-heptaldehyde, obtained from Schering–Kahlbauin, was distilled in *vacuo;* 82% of the total distillate boiled at a constant temperature. . The semicarbazone derivative of the aldehyde was prepared by treating 2 g. of the aldehyde with a water solution of 2 g. of semicarbazide hydrochloride and 2 g. of sodium acetate. Sufficient ethyl alcohol was then added to dissolve the aldehyde and the semicarbazone crystallized out in lustrous plate-like crystals which melted sharply at 109°.

The heptanones (methyl n-amyl ketone, ethyl n-butyl ketone, di-propyl ketone) were prepared by oxidation of the corresponding heptanols. To one mole of the alcohol, well cooled, was added one-sixth of a mole of potassium bichromate (8% solution). Then to the well-cooled mixture, a sixth of a mole of bichromate solution (8%) containing 1.5 moles of concentrated sulfuric acid was added dropwise. The reaction mixture was refluxed for one hour and a quarter at 70–80°. Water was added and the mixture distilled until all of the oil had distilled over. The oil was separated, washed three times with sodium carbonate and dried over calcium chloride. The crude yields were 85–90% of the theoretical.

The 2-heptanone was purified by making the sodium bisulfite addition product. The ketone was freed from the bisulfite compound by sodium carbonate and then distilled. Neither the 3-heptanone nor 4-heptanone formed sodium bisulfite addition products. The dried ketones were fractionated at atmospheric pressure and 60 to 70% of the products was constant boiling within *0.05'.

The semicarbazone of 2-heptanone was prepared and crystallized in fine lustrous crystals which, without purification, melted sharply at 123°. The semicarbazone from 3-heptanone crystallized in fine crystals somewhat granular in appearance. The semicarbazone, without purification, melted sharply at 89°. A second small fraction which crystallized out on long standing melted at 97–98'.

The semicarbazone from 4-heptanone crystallized in fine crystals, very similar in appearance to those obtained from 2-heptanone but very much less lustrous. These crystals, without purification, melted sharply at 132°.

Because of insufficient 4-heptanol the amount of 4-heptanone obtained was too small for the complete physical measurements. Dipropyl ketone

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[31] Blaise and Picard, *Ann. chim.*, [8] 25,266 (1912); *Chem. Zentr.*, *I*, 1208 (1912).

[32] Von Braun, ***Ann.*, 382,** 24 (1911).

[33] Dobriner, *ibid.*, 243, 28 (1888).

(purchased from Poulenc Frères) was dried and distilled. The total product boiled within less than one and one-half degrees and 70% was constant boiling within one-tenth of a degree. The boiling point of this compound and the melting point of its semicarbazone were identical with those obtained from the oxidation product of 4-heptanol. The physical constants of this product were measured.

TABLE V

PHYSICAL CONSTANTS

	Distillate, g.	Const. b. prod., g	Boiling point °C.	Mm.	M. p. semicarbazone, °C.	Density, t°/4° 15°	20°
n-Heptaldehyde	445	350	59.6 ± 0.05	30	108–109	0 8252	0.8219
2-Heptanone	87	58	150.2 ± 0.1	750	123	,0852	.8018
3-Heptanone	140	93	148 2 ± 0.05	756	89	.8222	.8183
4-Heptanone	82	58	144.0 ± 0 05	756	132	.8212	.8175

	Indices of refraction Helium red 17.5°	20°	Helium yellow 17.5°	20°	Helium green 17.5°	20°
n-Heptaldehyde	1 41051	1.40941	1.41315	1.41216	1.41748	1.41639
2-Heptanone	1.40760	1.40660	1 41027	1 40927	1.41433	1.41336
3-Heptanone	1.40750	1.40649	1.41017	1.40917	1.41423	1.41316
4-Heptanone	1.40560	1.40459	1.40818	1.40719	1.41218	1.41120

Literature Data

***n*-Heptaldehyde.**—B. p. (748.6 mm.) 152°, d^{16} 0.823;[24] b. p. (760 mm.) 155°, b. p. (20 m m) 54 4°, b. p. (22.5 mm.) 56.2°;[34] b. p. (10 mm.) 42–43°, d^{20} 0 8250, n_D 1.41655;[36] b. p. (18 mm.) 62°;[35] b. p. 152.2–153.2° (corr.), d_{15}^{15} 0.82264, d_{25}^{25} 0.81578;[37] b. p. 154.2–154.5°, d_4^{20} 0.8495, n_α^{20} 1.42339, n_D^{20} 1.42571, n_β^{20} 1.43094, n_γ^{20} 1.43514;[38] b. p. (759.3 mm.) 152.5–153.5°, $d_4^{19\ 9}$ 0.81708, $n_\alpha^{19\ 9}$ 1.41046, $n_D^{19.9}$ 1.41251, $n_\beta^{19\ 9}$ 1.41789, $n_\gamma^{19\ 9}$ 1.42236;[11] b. p. 154°, d_{19}^{19} 0.8320, n_α^{19} 1.41105, n_D^{19} 1.41370, n_γ^{19} 1.42312.[5]

Semicarbazone of ***n*-Heptaldehyde.**—M. p. 109°.[5]

Heptanone-2.—B. p. 151–152°;[13] b. p. (763 mm.) 151–152°, d^0 0.8366;[39] b. p. (760 mm.) 149.5–150°, d^0 0.8346;[40] b. p. 151–153°, d^{15} 0.8223;[41] b. p. (750 mm.) 148–151°;[42] b. p. 144–145°;[23] b. p. 148–150°;[43] b. p. (760 mm.) 151.45 ± 0.02°, d_0^4 0.83239, d_4^{15} 0.81966, d_4^{30} 0.80680, $n_{\mathrm{He\ red}}^{15}$ 1.40906, n_D^{15} 1.41156, $n_{\mathrm{He\ yellow}}^{15}$ 1.41161, $n_{\mathrm{He\ green}}^{15}$ 1.41577, $n_{\mathrm{He\ red}}^{25}$ 1.40481, n_D^{25} 1.40729, $n_{\mathrm{He\ yellow}}^{25}$ 1.40740, $n_{\mathrm{He\ green}}^{25}$ 1.41154.[22]

Semicarbazone of **2-Heptanone.**—M. p. 122–123°;[44] m. p. 122°;[10] m. p. 123°;[14] m. p. 122–123°;[40] m. p. 127°;[23] m. p. 121–123°;[4] m. p. 120°.[43]

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[34] Kahlbaum, *Ber.*, 17, 1251 (1884); 18, 2107 (1885).

[35] Schlotterbeck, *ibid.*, 40, 481 (1907).

[36] Semmler, *ibid.*, 42, 1161 (1909).

[37] Perkin, *J. Chem. Soc.*, 45,477 (1884).

[38] Briihl, *Ann.*, 203, 28 (1880).

[39] Behal, *Ann. chim.*, [6]15, 270 (1888).

[40] Moureu and Delange, *Bull. soc. chim.*, [3] 29, 674 (1903); *Compt. rend.*, 136, 753–756 (1903).

[41] Schimmel and Co., *Chem. Zentr.*, I, 1059 (1902).

[42] Johnson and Hager, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1927, Vol. VII, p. 60.

[43] Weizmann and Garrard, *J. Chem. Soc.*, 117,338 (1920).

[44] Dakin, *Am. Chem. J.*, **44,** 46 (1901).

Heptanone-3.—B. p. (742.9 mm.) 147–148°;[45] b. p. 149–150°;[14] b. p. (760 mm.) 147–148°;[23] b. p. 147.4°, m. p. −39°.[46]

Semicarbazone **of 3-Heptanone.**—M. p. 99–100°;[14] m. p. 103°;[23] m. p. 86–88°.[4]

Heptanone-4.—B. p. (760 mm.) 143.52°;[47] b. p. (760 mm.) 144–145°, d 0.8193, n_D 1.414;[48] b. p. 144.2°, m. p. −34°;[46] b. p. (770 mm.) 143–144°;[49] b. p. (755 mm.) 143.5–144.5°;[23] b. p. (68 mm.) 75.1;[50] d_4^{10} 0.8258, d_4^{30} 0.8105;[51] $d_{14\ 8}^{14\ 8}$ 0.8210;[52] $d_4^{15\ 1}$ 0.8205, $n_\alpha^{15\ 1}$ 1.40818, $n_\beta^{15\ 1}$ 1.41538;[53] $d_4^{21.7}$ 0.8160, n_α^{22} 1.40521, n_D^{22} 1.40732, n_γ^{22} 1.41650;[54] d_4^{20} 0.8217.[10]

Semicarbazone of **4-Heptanone.**—M. p. 133°;[55] m. p. 132°;[56] m. p. 132°;[57] m. p. 133°;[49] m. p. 129°;[23] m. p. 125°.[58]

The writer wishes to take this opportunity of expressing indebtedness to Professor Jacques Errera and to Professor Hector Van de Walle for the hospitality of their laboratories and appreciation for their suggestions in the prosecution of this work.

Summary

The four heptanols (1-, 2-, 3- and 4-), the four corresponding chlorides and four bromides, two of the iodides (1- and 3-), the n-heptaldehyde and the three ketones (keto-2, -3 and -4) have been investigated and some of the physical constants determined.

SOUTH HADLEY, MASSACHUSETTS

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[45] **Ponzio** and de Gaspari, *Gazz. chim. ital.*, **28,** II, 272 (1898).

[46] Timmermans, *Bull. soc. chim. Belg.*, 36, 502–518 (1927).

[47] Louguinine, *Ann. chim. phys.*, [7] 13, 331 (1898).

[48] **Amouroux** and **Murat,** *Compt. rend.*. 154,992 (1912).

[49] Henderson, Henderson and Heilbronn, *Ber.*, 47, 887 (1914).

[50] Rice, *Proc. Roy. Soc.* (London), **91,** 83 (1915).

[51] Morgan and Kramer, THIS JOURNAL, 35,1836 (1913).

[52] **Perkin, J.** *Chem. Soc.*, 69, 1173 (1896).

[53] Eijkman, *Rec. trav. chim.*, 12, 172 (1893); *Rech. Refrac.*, 86 (1919); *cf.* "Revue des Constants," Ref. 8.

[54] **Brühl, J.** *prakt. Chem.*, [2] 50, 141 (1894).

[55] Dilthey, *Ber.*, 34, 2123 (1901).

[56] Staudinger, *ibid.*, 44, 528 (1911).

[57] **Douris,** *Compt. rend.*, 157, 723 (1913).

[58] Lynn, THIS JOURNAL, 41,369 (1919).

[CONTRIBUTION FROM THE UNIVERSITÉ DE BRUXELLES, FACULTÉ DES SCIENCES APPLIQUÉES AND FROM MOUNT HOLYOKE COLLEGE, CHEMICAL LABORATORY]

AN INVESTIGATION OF A SERIES OF DERIVATIVES OF NORMAL HEPTANE. II. DIPOLE MOMENTS AND MOLECULAR CONSTITUTION[1]

BY JACQUES ERRERA AND MARY L. SHERRILL

RECEIVED DECEMBER 14, 1929 PUBLISHED MAY 8, 1930

The dipole moments of various aliphatic compounds containing one or more polar groups have been determined,[2] but it seemed advisable to study the effect on the moment of the position of the polar group in an aliphatic compound.

In order to have several different positions available a study of a series of derivatives of the straight chain heptane was begun, for in normal heptane it is possible to have a single substituent in four different positions in the molecule. The dipole moments of the four alcohols, heptanol-1 (n-heptyl alcohol), heptanol-2 (methyl-n-amyl carbinol), heptanol-3 (ethyl-n-butyl carbinol), heptanol-4 (dipropyl carbinol) have been measured. The three ketones, 2-heptanone (methyl-n-amyl ketone), 3-heptanone (ethyl-n-butyl ketone) and 4-heptanone (dipropyl ketone) have been prepared and purified and the moments of these and of the n-heptaldehyde have been determined. The chloro and the bromo derivatives corresponding to each of the heptanols have been synthesized and two of the iodo derivatives, 1-iodoheptane and 3-iodoheptane, have also been studied. Great care was taken in the preparation of these compounds to avoid any shift of position in the chain. The preparation of these derivatives and the proof of the position of the groups has been given by one of the authors.[3] The dipole moment of each of the compounds has been calculated from measurements of the dielectric constants of dilute solutions of the compound in a non-polar solvent, benzene, according to the well-known method

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[1] A preliminary report of this work was made at a Symposium in Leipzig, June, 1929, and has been published, p. 41, in "Dipolmomente und Chemische Struktur," herausgegeben von Professor P. Debye, Verlag von S. Hirzel, Leipzig, **1929**. See also Ref. 1, preceding article, M. L. Sherrill, THIS JOURNAL, **52,** 1982 (1930).

[2] (a) Debye, "Polare Molekeln," pp. 39, 45, 52, 59, etc., p. 191 (complete tables), Leipzig, **1929,** "Polar Molecules," New York, **1929** (less complete data); (b) Errera, *J. phys.*, [6] *6,* 390 (1925); *Compt. rend.*, **182,** 1623 (1926); *Physik. Z.*, 27,764 (1926); **29,** 689 (1928); "Polarization Dielectrique," Presses Universitaires, Paris, **1928;** (c) Ghosh, *Nature,* **123,** 413 (1929); *C. A.*, **23,** 3383 (1929); (d) Gross, *Physik. Z.*, **30,** 504 (1929); (e) Höjendahl, "Dissertation," Kopenhagen, **1928** (tables and bibliography); (f) Lange, *Z. Physik*, **33,** 169 (1925); (g) Sanger, *Physik. Z.*, **27,** 556 (1926); (h) Smyth, THIS JOURNAL, 46, 2151 (1924); **51,** 2380 (1929); (i) Smyth and Morgan, *ibid.*, **50,** 1547 (1928); (j) Smyth and Stoops, *ibid.*, **51,** 3312 (1929); (k) Williams, *Physik.* Z., **29,** 174 (1928); *Z. physik. Chem.*, **138A,** 75 (1928); (l) Wolf, ibid., **2B,** 39 (1929).

[3] M. L. Sherrill, THIS JOURNAL, **52,** 1982 (1930).

shown by Debye.[4] The resonance method was used and the wave length was 100 meters. The capacity measurements were of a precision of 1 part in 500.

The total polarization of a pure substance is regarded as made up of three parts, the polarization P_E caused by electronic shifts induced in the molecule, the polarization P_A attributed to atomic shifts and P_P, the polarization due to orientation of the permanent dipoles in the molecule.[5] The total polarization is determined according to the equation $P = \epsilon - 1/\epsilon + 2 \cdot M/d$, in which ϵ is the dielectric constant, M is the molecular weight and d is the density of the compound. P_∞ is the total polarization of the unassociated molecule obtained by extrapolation of $P_{1,2}$ and P_2 from the data of the dilute benzene solutions, in which $P_{1,2} = \epsilon - 1/\epsilon + 2 \cdot C_1M_1 + C_2M_2/d$ and $P_2 = P_{1,2} - C_1P_1/C_2$. Since it was not possible, at this time, to measure the refractive indices in the long waved infra-red, instead of measuring $P_E + P_A$, P_E was determined from the refractive index of the compounds obtained by measuring the helium yellow line at 20°. P_E is considered equal to the molecular refractivity RM as defined by the Lorenz-Lorentz law, $P_E = n^2 - 1/n^2 + 2 \cdot M/d$, in which n is the refractive index, M the molecular weight and d the density. The dipole moment μ is calculated according to Debye,[6] $\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - P_E)T}$.

According to one of the authors,[7] the molecular association in a liquid may be considered as the result of two factors. The first is the dipolar molecular association which may be attributed to the electrostatic forces of the permanent dipoles in the molecule, these forces being determined by the size and position of the dipoles in the molecule and the form of the molecule itself. The second is the molecular association of the molecules which are not dipoles, which may be the result of intermolecular attraction as indicated by van der Waals. The total association, the sum of these two factors, must be determined by measurements such as vapor pressure, viscosity and surface tension. Polarization measurements, which give the electric moment in unit volume, are able only to give some insight into the first factor of this association corresponding to the association of the dipoles. In fact, in the consideration of the total polarization, $P = P_E + P_A + P_P$, Debye has shown that $P_E + P_A$ corresponds to the polari-

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[4] P. Debye, *Handbuch der Radiologie*, **6**, 597 (1925); "Polare Molekeln," Leipzig, 1929, p. 46; "Polar Molecules," New York, 1929, p. 44.

[5] J. Errera, "Polarization Dielectrique," Les Presses Universitaire de France, 1928.

[6] P. Debye, "Polare Molekeln," Leipzig, 1929, p. 51; "Polar Molecules," New York, 1929, p. 49.

[7] J. Errera, *Z. physik. Chem.*, **138A,** 332 (1928); **140A,** 273 (1929); "Dipolmomente und Chemische Struktur," herausgegeben von P. Debye, Leipzig, 1929, p. 105; "L'Activation et la Structure des Molecules," Réunion Internationale de Chimie-Physique, Paris, 1928, p. 236.

zation of those constituents whose field is determined by the van der Waals molecular attraction. For a substance whose molecules are not dipoles and whose total polarization is limited to $P_E + P_A$ it is not possible to determine the association through polarization measurements. Where, however, there are dipole molecules present, the association of the permanent dipoles affects greatly the P_P factor. It is then possible to determine the dipolar association, y, of the permanent dipoles present by the ratio of the total polarization at infinite dilution of the permanent dipoles, $P_{P\infty}(P_{P\infty} = P_, - P_E)$, to the total polarization of the permanent dipoles in pure state, P_P $(P_P = P - P_E)$, or $P_{P\infty}/P_P = y$. In the data for the various series of compounds tabulated below, P_E is a first approximation in place of $P_E + P_A$. The probable error in the dielectric measurements is 0.5%.

TABLE I

CONSTANTS OF HEPTANE DERIVATIVES AT 22°

Derivative	d_4	ϵ	P	P_∞	P_E	$\mu \times 10^{18}$	y
Heptanol-1	0.8214	12.10	110.90	98.0	36.08	1.71	0.83
Heptanol-2	.8153	9.21	104.30	97.5	36.07	1.71	.90
Heptanol-3	.8194	6.86	93.69	97.5	35.98	1.71	1.07
Heptanol-4	.8170	6.17	89.97	97.0	35.96	1.70	1.13
Heptaldehyde	.8206	9.07	101.40	172.8	34.64	2.56	2.06
Heptanone-2	.8006	9.77	106.20	176.0	35.21	2.59	1.98
Heptanone-3	.8167	12.88	111.60	197.0	34.49	2.78	2.11
Heptanone-4	.8160	12.43	110.80	190.0	34.39	2.72	2.04
1-Chloroheptane	.8702	5.48	92.65	111.4	39.50	1.85	1.34
2-Chloroheptane	.8651	6.52	100.60	126.3	39.50	2.03	1.42
3-Chloroheptane	.8674	6.70	101.40	127.0	39.47	2.04	1.41
4-Chloroheptane	.8694	6.54	100.20	127.2	39.40	2.04	1.44
1-Bromoheptane	1.1342	5.38	93.71	113.2	42.39	1.85	1.40
2-Bromoheptane	1.1255	6.46	102.70	131.8	42.50	2.06	1.48
3-Bromoheptane	1.1341	6.93	104.80	130.0	42.42	2.04	1.40
4-Bromoheptane	1.1330	6.81	104.10	130.3	42.40	2.04	1.42
1-Iodoheptane	1.3736	4.90	93.03	117.0	47.60	1.84	1.53
3-Iodoheptane	1.3656	6.39	106.40	126.3	47.99	1.93	1.34

The results show that in the case of the hydroxy group in straight-chain hydrocarbons, such as the heptanols, the dipole moment is independent of the position of the polar group in the chain. It is also to be noted that the association is greatest in the case of 4-heptanol and decreases in order to 1-heptanol, which is least associated, for the dipole moment of each of the four alcohols is the same and the density practically the same, yet the dielectric constant which should be the same varies from $\epsilon = 6.2$ in 4-heptanol to $\epsilon = 12.1$ in the case of 1-heptanol. In the carbonyl derivatives, one of which is an aldehyde, the other three being ketones, it is found that the dipole moment of the 1-derivative, n-heptaldehyde, is smaller than that of the 3- and 4-heptanones. The 2-heptanone instead of being like the 3- and 4-derivatives has a dipole moment more like that of *n*-heptaldehyde. This seems to correspond somewhat to the chemical reactivity, for of these compounds only the aldehyde and the 2-heptanone form bisulfite addition products. The dipole moments of a number of ketones have been determined by Wolf,[8] and dipropyl ketone is one of these for which he found a value of $\mu \times 10^{18}$ of 2.73, which checks the value obtained in this work.

In the case of the halogen derivatives it is seen that in the 2-, 3- and 4-positions the dipole moment is practically independent of the position in the chain. In 1-chloro-, 1-bromo- and 1-iodoheptane the dipole moment is smaller than that of the other halogen derivatives. The dipole moment of n-heptylbromide is given by Smyth[9] as 1.86, which compares favorably with the value found in this work. From the data obtained with these halogen compounds of heptane it is to be inferred that the dipole moment is the same for the chloro, bromo and iodo derivatives of the aliphatic compounds as Williams[10] has found for the chloro and bromo derivatives of aromatic compounds, the numerical value, however, being greater than for the aromatic derivatives. For the disubstituted chlorides and bromides of benzene and of ethylene one of the authors[11] has found that the moment of the chloro derivatives was larger than that of the bromo and of the bromo larger than the iodo derivatives. In these heptane derivatives the dipole moment of the halogen compounds has been found to be greater than that of the hydroxyl derivative, which is different from that found for aromatic compounds,[10] where the dipole moment of the hydroxy derivative is greater than that of the halogen derivative. The characteristic moment of the polar substituents in n-heptane are tabulated below. The values are approximate in the sense that P_A, which in certain cases has a value which cannot be neglected, has not been taken into consideration.

TABLE II

CHARACTERISTIC MOMENTS ($\mu \times 10^{18}$) OF POLAR SUBSTITUENTS IN *n*-HEPTANE

Group	OH	H—C=O	C=O	Cl	Br	I
First position	1.70	2.55	(2.58) (2-ketone)	1.85	1.85	1.80
Other position	1.70	..	2.75	2.00	2.00	1.90

In addition to the alcohol derivatives of heptane there were available three of the petanols (n-amyl alcohol,[12] methyl propyl carbinol and diethyl carbinol). The dielectric constants of these alcohols were measured and the dipole moments calculated as in the case of the heptane derivatives.

Here as in the heptanols it is evident that the moment is independent of

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[8] K. L. Wolf, *Zeit. physik. Chem., 2B,* 39 (1929).

[9] C. P. Smyth, THIS JOURNAL, 51, 2385 (1929).

[10] J. W. Williams, *ibid.*, 50, 2350 (1928).

[11] J. Errera, *J. phys.*, 6, 390 (1925).

[12] Obtained from Professor Timmermans, University of Brussels.

TABLE III

PENTANE DERIVATIVES AT 22°

Derivative	d_4	ϵ	P	P_∞	P_E	$\mu \times 10^{18}$	y
Pentanol-1	0.8134	14.37	88.53	84.0	26.80	1.65	0.93
Pentanol-2	.8100	13 82	88.43	86.0	26.88	1.66	.94
Pentanol-3	.8142	13.02	86.82	83.0	26.52	1.64	.94

the position of the substituent in the molecule; the numerical value of the moment, 1.65, is, however, slightly smaller than that obtained for the heptanols, 1.70. Representative data on electric moments of the straight-chain alcohols as given in the literature are as follows: methyl alcohol, 1.73 (gas),[2e] 1.64 (solution);[13] ethyl alcohol, 1.63,[10] 1.72,"' 1.64;[14] n-propyl alcohol 1.66,[14] 1.53;[2f] n-butyl alcohol 1.65,[2f] 1.75;[2j] octyl alcohol 1.71.[2j] A comparison of these values with the electric moments of the C_5 and C_7 alcohols obtained in this study shows fairly good agreement.

Summary

Dielectric constant data have been obtained for the following compounds, pure and in benzene solution: four straight-chain heptanols, the n-heptaldehyde, the three ketones, the four chloro and four bromo derivatives and 1-iodo and 3-iodoheptane. From these data the electric moments have been determined.

The position of the polar group in the chain in the case of the alcohols has been found to have no effect. In the case of the halogen derivatives, the moment is found to be the same for chloro, bromo and iodo compounds but a slightly smaller moment is obtained when the substituent is in the 1-position than when it is in either of the other positions.

The electric moment characteristic of each of the groups, hydroxyl carbonyl and halogen, as shown in aliphatic compounds has been tabulated.

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[13] Stranathan, *Phys. Rev.*, 31, 653 (1928).

[14] Debyc, *Handbuch der Radiologie*, **6**, 390 (1925).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

STUDIES ON THE POLYMETHYLBENZENES. III. THE VAPOR PRESSURES OF THE TETRAMETHYLBENZENES, AND OF PENTA- AND HEXAMETHYLBENZENE

BY F. H. MACDOUGALL WITH LEE IRVIN SMITH

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No data are recorded in the literature on the vapor pressures of any of the polymethylbenzenes containing four or more methyl groups, and the work reported in this paper deals with the determination of the vapor pressure curves of five polymethylbenzenes: the three tetramethylbenzenes, penta- and hexamethylbenzene. Only the vapor pressures of the liquid hydrocarbons have been measured: the lower limit is either around room temperature, or as close to the melting point of the hydrocarbon as could be obtained with the apparatus used.

The purification of all the materials is given in a previous paper.[1] In every case except one the purest materials at hand were used, judging by the freezing point curve. The one exception is in the case of prehnitene (1,2,3,4-tetramethylbenzene), the vapor pressure sample showing a freezing point of $-6.8°$ as compared with a later sample purified through the picrate, and which showed a freezing point of $-6.4°$. However, the boiling point of this very pure sample was determined at two or three pressures and the results were found to check within the experimental error the values given by the sample freezing at $-6.8°$, so that it was not felt necessary to re-check the whole curve.

Apparatus and Procedure.—The procedure followed was to determine the boiling point under various pressures in a modified Claisen flask, arranged so that the distillate was returned to the flask. Superheating was avoided by passing a very fine stream of air through the boiling liquid, and the temperature of the outside (Wood's metal) bath was carefully regulated so that a nice even distillation resulted. The neck of the flask was made long enough so that the thermometer was completely immersed in the vapor, and was wide enough so that the thermometer did not touch the flask at any point. The thermometers used were all standardized. The pressure was read on a closed tube manometer, internal diameter about 7.5 mm., which had a range up to atmospheric, and which had been carefully checked against an accurately calibrated manometer. The accuracy of reading the manometer scale was about 0.3 mm., but since two readings were necessary in order to determine the pressure, the error in any given reading was double this, or about 0.5 mm. The pressure was varied by inserting a long tapering capillary into the line and cutting off small lengths in passing from one determination to the next.

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[1] Smith and MacDougall, THIS JOURNAL, 51, 3001 (1929).

With a good pump having high capacity, this method permits the pressure to be changed easily and very constant readings were obtained. In every case the readings were checked: first the pressure was read, then the temperature, and after half a minute these readings were repeated in the reverse order.

Results.—The results are given in the tables and curves. Figure 1 is taken from the observed data directly, plotting alternate readings in order to simplify drawing these curves. In addition, the curves for durene and isodurene are so close together that only one of them has been drawn,

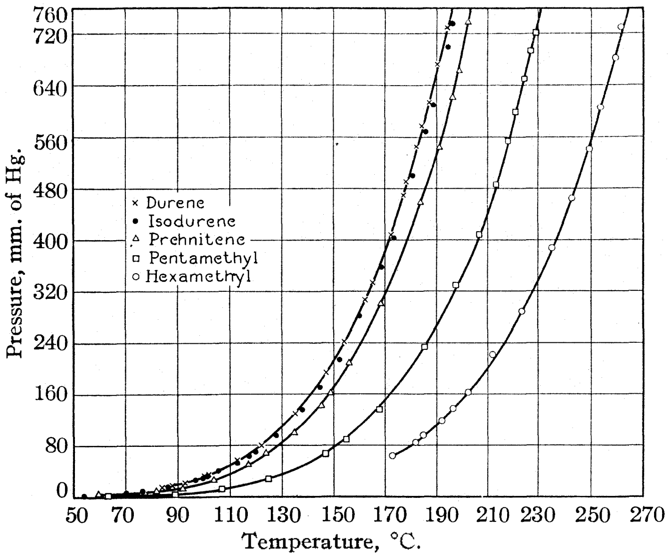


Fig. 1.—Vapor pressure curves of the polymethyl benzenes.

TABLE I

VAPOR PRESSURE EQUATIONS, $u = 1000/T$

Durene $\log_{10} P = 18.8224 - 3093/T - 3.499 \log_{10} T$

Isodurene $\log_{10} P = 5.9514 - 0.6033\, u - 0.3972\, u^2$

Prehnitene $\log_{10} P = 6.4470 - 1.0542\, u - 0.3099\, u^2$

Penta $\log_{10} P = 6.7125 - 1.323\, u - 0.309 u^2$

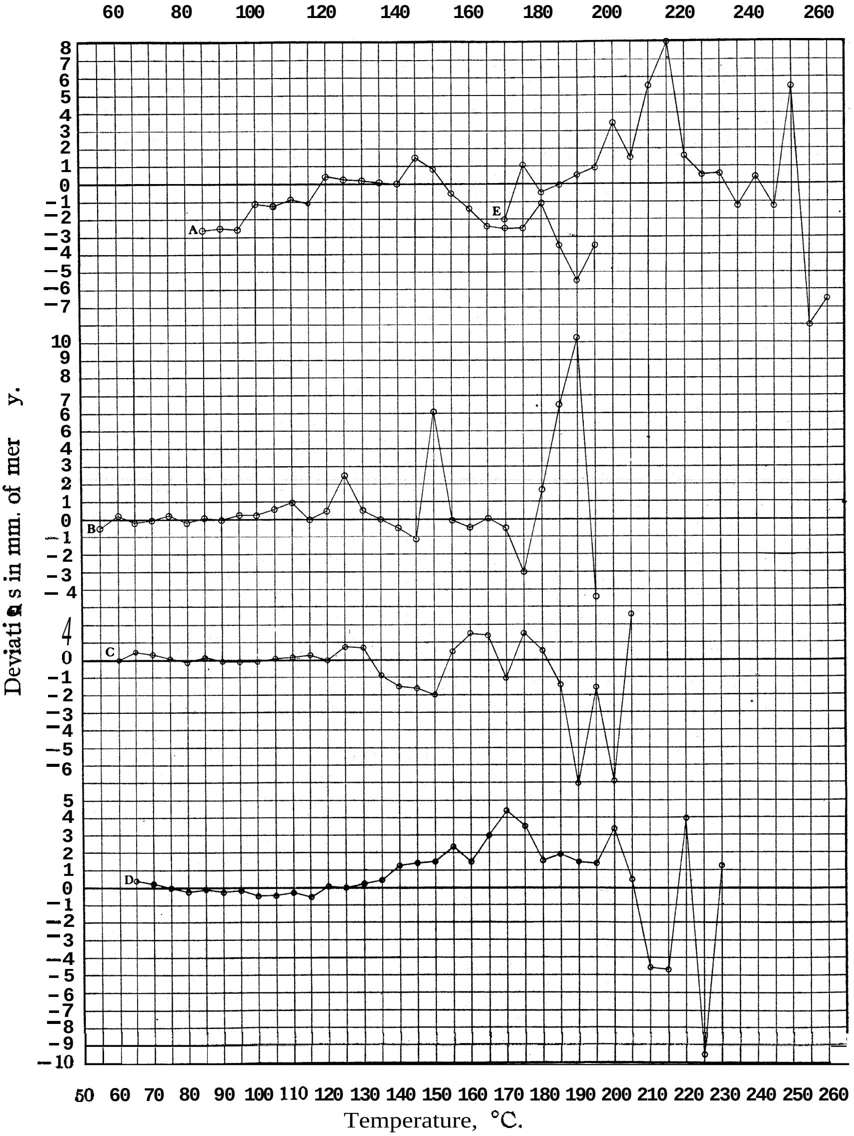
Hexa $\log_{10} P = 7.7760 - 2.4394\, u - 0.1009\, u^2$

TABLE II

CONSTANTS

Substance	T_{760}	L_{760}	$\frac{L_{760}}{T_{760}}$
Durene	469.0	10,880	23.2
Isodurene	471.1	10,470	22.2
Prehnitene	477.6	10,760	22.5
Penta	505.0	11,650	23.1
Hexa	536.7	12,870	24.0

the points on the other merely being indicated. Table I gives the empirical equations for the vapor pressures. Figure 2 gives the deviations of the calculated pressures from the observed values. These deviations,



A, Durene; B, isodurene; C, prehnitene; D, pentamethylbenzene; E, hexamethylbenzene.

Fig. 2.—Deviation plots for the vapor pressures of the polymethylbenzenes. Positive deviations are to be added to the calculated to find the observed. Negative vapor pressures are to be added.

when positive, are to be added to the calculated pressures, and subtracted when negative. Table II gives the normal boiling point, the latent heats of vaporization, and L/T, or the "entropy of vaporization." All pressure readings are in mm. of mercury at 0°, and all temperatures are corrected.

Summary and Conclusions

1. The vapor pressures of all the polymethylbenzenes containing four or more methyl groups have been determined over a considerable range of temperatures, and the results are given in the form of tables and curves.
2. From these data, the latent heats of vaporization have been calculated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXV. ALKYLATION ON NITROGEN OF THE PYRIMIDINE CYCLE BY APPLICATION OF A NEW TECHNIQUE INVOLVING MOLECULAR REARRANGEMENTS

BY GUIDO E. HILBERT[1] AND TREAT B. JOHNSON

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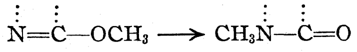
That the *lactim* ethers I will undergo rearrangements to their isomeric and stable *lactam* configurations II has been known for a long time. These transformations are not reversible and are brought about by the application of heat or through the influence of special catalytic agents, and have been observed to take place in both the acyclic and cyclic series of organic compounds.[2]



$$N{=}C{-}OCH_3 \longrightarrow CH_3N{-}C{=}O$$

I II

The interesting data obtained by Knorr as a result of his study of molecular transformations in the pyrazolone and quinoline series suggested that corresponding changes might be brought about in pyrimidine combinations containing *lactim* ether groupings[3] Knorr showed that certain a- and γ-alkoxyquinolines interact with methyl iodide with formation of addition products IV which are unstable and break down on heating to form N-alkylquinolones V. The transformation of the ethoxyquinoline

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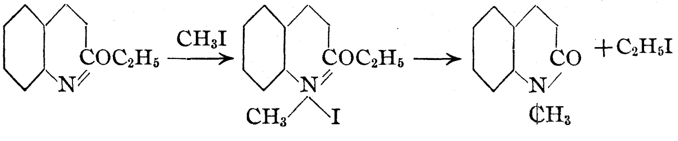
[1] Sterling Research Fellow, 1928–1930.

[2] A review of the literature on imido-ester rearrangements has been recorded in the following publications: Johnson and Hahn, "Theories of Organic Chemistry (Henrich)," John Wiley and Sons, Inc., New York, **1922**, and in "Molecular Rearrangements," by C. W. Porter, American Chemical Society Monograph No. 45, The Chemical Catalog Company, Inc., New York, **1929**. See also Chapman, *J. Chem. Soc.*, 569 (1929).

[3] Knorr, ***Ann.***, **293**, **5** (1896); *Ber.*, **30**, 922, 927, 937 (1897); see also Lieben and Haitinger, *Monatsh.*, 6,315 (1885), for rearrangement of alkoxypyridines.

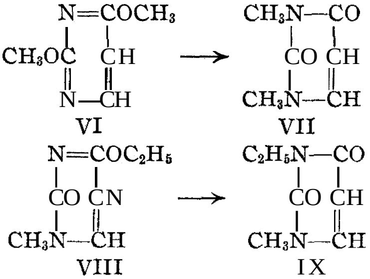
III into the corresponding N-methyl derivative (lactam construction) is expressed by the following formulas. Knorr also found that the *lactim*



III IV V

constructions 111 are rearranged by heating, forming the isomeric *lactams* in good yield.

Substituted pyrimidines of the type represented by the 2,6-dialkoxypyrimidines are analogous in constitution to the quinoline *lactim* compounds studied by Knorr. Several pyrimidine ether constructions of this type have been prepared,[4] but in no case has any tendency to undergo molecular rearrangements been observed, nor has the behavior of these compounds toward alkyl iodides been investigated. We have had occasion to investigate the properties of certain representatives of this series and we find that the 2,6-dialkoxypyrimidines and constructions like 2-oxy-3-alkyl-6-alkoxypyrimidines easily undergo rearrangement on heating to form the 1,3-dialkyluracils in excellent yields. The respective changes are expressed by the following formulas.



VI VII

VIII IX

These rearrangements open up a new technique for synthesizing N-alkylated uracils of known structure which hitherto have been very difficult to obtain in a pure condition. Thus far it has been impossible to produce a partial rearrangement by heating a 2,6-dialkoxypyrimidine leading to the formation of derivatives in which only one *lactim* grouping has been destroyed. 1,3-Dialkylpyrimidines are always the end-products of pyrolysis.

Pyrimidines representing the partially rearranged forms are obtained by the action of alkyl halides. The interaction of methyl iodide with 2,6-dimethoxypyrimidine VI at room temperature, for example, yields smoothly 2-oxy-3-methyl-6-methoxypyrimidine. In other words, the two

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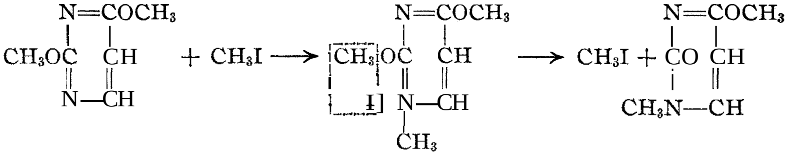
[4] Schlenker, Ber., 34, 2812 (1901); St. Augerstein, *ibid.*, 34, 3956 (1901); Buttner, *ibid.*, 36,2227 (1903); Gabriel and Colman, *ibid.*, 36, 3379 (1903); Johnson and Joyce, THIS JOURNAL, 37,215 (1915); Johnson and Moran, *ibid.*, 37,2591 (1915).

lactim configurations within the same pyrimidine molecule differ in their stability, and the nitrogen atom which is alkylated during the molecular changes is that one which is the most basic, or the nitrogen in position 3 of the pyrimidine ring. The mechanism of the reaction, which is practically quantitative, is easily explained by assuming the primary formation of an addition product with methyl iodide. This intermediate pentavalent nitrogen compound X being unstable, dissociates with the production of the 3-nitrogen derivative XI and a new alkyl halide by coupling of the *lactim* alkyl group with iodine. These changes are expressed by the formulas



VI X XI

That an intermediate addition product as expressed by formula X represents one stage of our reaction is supported by the behavior of 2,6-diethoxypyrimidine toward methyl iodide. In this case the product of the reaction was 2-oxy-3-methyl-6-ethoxypyrimidine, but we were unable to identify any substance corresponding to an addition compound. That such addition compounds, are exceedingly unstable was shown by the behavior of 2,6-dimethoxypyrimidine toward methyl iodide at ordinary temperature in quantities very much less than molecular proportions of the halide. Under these experimental conditions the dimethoxy compound was completely transformed into 2-oxy-3-methyl-6-methoxypyrimidine XI in a few days. This interesting result is direct evidence that the addition product is an unstable configuration, breaking down as soon as formed and continually regenerating the halide, thus allowing the reaction to go to completion.

In the above reactions methyl iodide was found to be much more reactive than ethyl iodide, and the use of benzene as a solvent decreased the rate of reactivity very appreciably, which is in accord with the recent work of Norris and Prentiss.[5] It is also a well-known fact that alkyl halides show a much greater tendency to add to basic nitrogen groupings than the corresponding alkyl bromides or chlorides. In the case of 2,6-diethoxypyrimidine, for every molecule of methyl iodide interacting with this compound, one molecule of ethyl iodide is liberated. However, since methyl iodide is in excess and is also the more reactive halide, the main product formed is 2-oxy-3-methyl-6-ethoxypyrimidine with the practical exclusion of 2-oxy-3-ethyl-6-ethoxypyrimidine.

The 2-oxy-3-alkyl-6-alkoxypyrimidines very easily undergo hydrolysis

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[5] Norris and Prentiss, THIS JOURNAL, **50**, 3042 (1928).

by treatment with hydrochloric acid, yielding mono alkylated uracils quantitatively. This new reaction, which makes possible the application of a new technique for the preparation of 2,6-dioxypyrimidine compounds alkylated in position **3,** promises to assume an important biochemical significance. By application of this new procedure it should be possible to synthesize sugar derivatives of pyrimidines related structurally to the nucleosides found in nucleic acids. In fact, we have already found that the hexose derivative—bromotetra-acetylglucose—interacts smoothly with 2,6-dimethoxypyrimidine giving a crystalline compound exhibiting the properties of a true nucleoside derivative.[6] This special reaction is now under investigation and the results of our research will be reported in a future paper from this Laboratory.

Experimental Part

The Preparation of 2,6-Dialkoxypyrimidines.—The chlorine atoms occupying the 2- and 6-positions in the pyrimidine ring are very reactive and interact practically instantaneously with sodium alcoholates to give the corresponding 2,6-dialkoxypyrimidines in excellent yields.

2,6-Dimethoxypyrimidine, $\overline{\mathrm{N{=}C(OCH_3)N{=}C(OCH_3)CH{=}C}}\mathrm{H}$.—This compound has been described previously by Gabriel and Colman,[7] who prepared it by reduction of 2,6-dimethoxy-4-chloropyrimidine. They report a boiling point of 204.5–205° and a melting point at about 10°. Their method, however, is an impractical one for quantity production and we recommend the following. Forty grams of 2,6-dichloropyrimidine[8] are dissolved in 200 cc. of absolute methyl alcohol[9] and added slowly to a solution of 12.5 g. of sodium in 200 cc. of dry methyl alcohol. A vigorous reaction immediately takes place, sodium chloride precipitating and the mixture generating sufficient heat to raise the temperature of the solution to its boiling point. The reaction is complete within a few minutes. After filtering off the sodium chloride, the excess of alcohol is then expelled by distillation under reduced pressure and the residual oil treated with 100 cc. of 30% sodium hydroxide solution. The dimethoxypyrimidine separates as the upper layer and is extracted by ether, dried over sodium sulfate and finally purified by distillation. Our product distilled as a colorless oil boiling at 202°, and solidified on cooling. The compound melts at 17.5° and the yield is 35 g. or 93% of the theoretical.

Anal. Calcd. for $C_6H_8O_2N_2$: N, 20.00. Found: N, 19.72, 19.85.

2,6,-Diethoxypyrimidine, $\overline{\mathrm{N{=}C(OC_2H_5)N{=}C(OC_2H_5)CH{=}C}}\mathrm{H}$.—The procedure for obtaining this pyrimidine was similar to that described above. It was produced as a colorless oil boiling at 224–225° and melting at 19–20'. The yield was 85% of the theoretical.

Anal. Calcd. for $C_8H_{12}O_2N_2$: N, 16.67; H, 7.14; C, 57.14. Found: N, 16.27, 16.67; H, 7.21; C, 56.92.

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[6] Johnson and Hilbert, *Science,* 69, 579 (1929).

[7] Gabriel and Colman, *Ber.,* 36, 3379 (1903).

[8] Hilbert and Johnson, THIS JOURNAL, 52,1152 (1930).

[9] On dissolving 2,6-dichloropyrimidine in methyl alcohol heat should not be applied as this initiates a reaction with replacement of halogen and formation of the dialkoxypyrimidine. The latter compound undergoes hydrolysis in the presence of the generated hydrochloric acid and is changed immediately into uracil.

Rearrangement of Alkoxypyrimidines

Rearrangement of **2,6-Dimethoxypyrimidine** to **1,3-Dimethyluracil.**—Four and one-half grams of the dimethoxypyrimidine is heated in an oil-bath at 220–240° for four hours. At first there is vigorous ebullition which gradually subsides and finally ceases as the proportion of rearranged compound increases. On cooling, the pale brown reaction product completely solidified. This was purified by dissolving in a mixture of alcohol and ether and allowing to cool after decolorization with norite. The yield of rearranged pyrimidine was 4 g. and it crystallized in colorless prisms melting at 123–124". A mixture of this substance with a sample of 1,3-dimethyluracil prepared by a known method[10] melted at the same temperature.

Rearrangement of 2-Oxy-3-methyl-6-methoxypyrimidine to **1,3-Dimethyluracil.**—This change is accomplished by heating under the same conditions that were employed for the molecular rearrangement of 2,6-dimethoxypyrimidine to dimethyluracil. The purified 1,3-dimethyluracil melted at 123–124° and the yield was excellent.

Rearrangement of 2-Oxy-3-methyl-6-ethoxypyrimidine to I-Ethyl-3-methyluracil, $CH_3N—CO—N(C_2H_5)COCH=CH$.—After heating 5 g. of the above ethoxypyrimidine in an oil-bath at 250" for eight hours, the resulting dark brown reaction product was extracted with ether, dried and purified by distillation under diminished pressure. The rearranged pyrimidine was obtained as a colorless oil boiling at 140–141° at 4 mm. which solidified on cooling. It melted at 60–61°. The yield was 4 g. This pyrimidine is very soluble in water, alcohol and ether and sparingly soluble in ligroin. It gives a negative Wheeler and Johnson color test.[11]

Anal. Calcd. for $C_7H_{10}O_2N_2$: N, 18.18; H, 6.49; C, 54.55. Found: N, 18.26, 18.43; H, 6.67; C, 54.64.

The Action of Alkyl Iodides on Alkoxypyrimidines from Uracil

2-Oxy-3-methyl-6-methoxypyrimidine, $CH_3NCON=C(OCH_3)CH=CH$.—Five grams of 2,6-dimethoxypyrimidine was mixed with 10 g. of freshly distilled methyl iodide and the solution allowed to stand at room temperature.[12] Within two to three hours large colorless crystals started to deposit in the solution, and in twelve hours the reaction was complete. The reaction product was separated by filtration and washed with ether. It was purified by recrystallization from warm alcohol and separated, on cooling, in the form of colorless prisms which melted at 149–150°. The yield of rearranged pyrimidine was quantitative. The compound is very soluble in alcohol and water and insoluble in benzene and ether.

Anal. Calcd. for $C_6H_8O_2N_2$: N, 20.00; H, 5.71; C, 51.43. Found: N, 19.98, 20.13; H, 5.82; C, 51.40.

The structure of this compound was established by its behavior on hydrolysis. When dissolved in dilute hydrochloric acid and the solution evaporated on a steam-bath it was converted quantitatively into 3-methyluracil melting at 237–238°.[13]

Anal. Calcd. for $C_5H_6O_2N_2$: N, 22.22. Found: N, 22.21, 22.19.

An experiment was carried out using the same quantities of 2,6-dimethoxypyrimidine and methyl iodide as given above. The solution, however, was diluted with

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[10] Davidson and Baudisch, THIS JOURNAL, 48, 2379 (1926).

[11] Wheeler and Johnson, *J. Biol. Chem.*, 3,183 (1907).

[12] It is preferable to carry out this reaction in the dark and thereby reduce to a minimum the quantity of colored products formed during the reaction.

[13] Wheeler and Johnson, *Am.* Chem. J., 42, 30 (1909).

benzene. The effect of this was to decrease the rate of reaction enormously. as the rearrangement required several weeks to go to completion. The reaction was furthermore highly colored.

In a second experiment 5 g. of 2,6-dimethoxypyrimidine was mixed with two droplets of methyl iodide and the solution sealed in a tube. In two days the rearrangement was complete, giving a quantitative yield of 2-oxy-3-methyl-6-methoxypyrimidine. If two drops of ethyl iodide are substituted for the methyl iodide, similar results are obtained except that in this case the reaction requires several weeks for completion.

2-Oxy-3-Methyl-6-Ethoxypyrimidine, $CH_3\overline{NCON{=}C(OC_2H_5)CH{=}CH}$.—Five grams of 2,6-diethoxypyrimidine dissolved in 10 g. of methyl iodide was converted completely at room temperature and within ten hours into the above pyrimidine. It was purified by recrystallization from a mixture of alcohol and ether and separated as colorless plates melting at 136°. This pyrimidine is very soluble in alcohol and water and insoluble in ether. The yield was excellent and no trace of a pyrimidine containing an ethyl group substituted on nitrogen of the pyrimidine cycle was detected.

Anal. Calcd. for $C_7H_{10}O_2N_2$: N, 18.18; C, 54.5; H, 6.49. Found: N, 18.33, 18.20; C, 54.68; H, 6.33.

When this compound was warmed in hydrochloric acid solution it was converted quantitatively into 3-methyluracil.

1,3-Diethyluracil, $C_2H_5\overline{NCON(C_2H_5)COCH{=}CH}$.—This was formed by refluxing 2,6-diethoxypyrimidine (5 g) with ethyl iodide (10 g.) for one week. The excess of the iodide was then removed with a blast of air and the residue distilled under diminished pressure. It boiled at 135° at 4 mm. and the yield of pyrimidine was 4 g. 1,3-Diethyluracil is a colorless, odorless oil which solidifies on cooling and melts at 14–15°. It gives a negative Wheeler and Johnson color test.[11]

Anal. Calcd. for $C_8H_{12}O_2N_2$: N, 16.67; C, 57.14; H, 7.14. Found: N, 16.27, 16.67; C. 56.86; H, 7.48.

This rearrangement to diethyluracil is also brought about by heating the 2,6-diethoxypyrimidine in a bomb tube at 260" for twenty-four hours. The product of the reaction was a dark brown viscous oil. This was dissolved in ether, dried over sodium sulfate and purified by distillation. The yield was 4 g. of a colorless oil boiling at 290–295°.

Anal. Calcd. for $C_8H_{12}O_2N_2$: N, 16.67. Found: N, 16.55, 16.33.

1,3-Diethyluracil has not been described previously in the literature and as we wished to compare the properties of our new compound with a sample prepared by a different method, an alkaline solution of uracil was alkylated by interaction with diethyl sulfate according to the technique employed by Davidson and Baudisch[10] for the preparation of 1,3-dimethyluracil. Twenty grams of uracil and 17 g. of sodium hydroxide were dissolved in 100 cc. of water, warmed to 30° and 45 cc. of diethyl sulfate was added slowly with constant agitation. The reaction mixture, after standing for one hour, was finally heated to boiling and then cooled. This solution was then repeatedly extracted with chloroform to remove 1,3-diethyluracil. This was purified by distillation as described above and agreed in all its properties with the pyrimidine obtained by rearrangement of the 2,6-diethoxypyrimidine. The yield was 10 g.

1,3-Diethyl-5-bromo-uracil, $C_2H_5\overline{NCON(C_2H_5)COCBr{=}CH}$.—This is formed by dissolving the 1,3-diethyluracil in absolute alcohol and then adding to the solution the required amount of bromine. The alcohol was evaporated on a steam-bath and the bromopyrimidine left behind purified by crystallization from water. It separated in prisms melting at 80–81°. Depending on the conditions of crystallization it sometimes separates as colorless needles and at other times as colorless rhombic blocks. In one experiment a modification was obtained which melted at 71°; after resolidifying the melting point rose to 80–81°.

Anal. Calcd. for $C_8H_{11}O_2N_2Br$: N, 11.34. Found: N, 11.45, 11.38.

Summary

1. 2,6-Dialkoxypyrimidines are formed smoothly by interaction of 2,6-dichloropyrimidine with sodium alcoholates.

2. The 2,6-dialkoxypyrimidines and the 2-oxy-3-alkyl-6-alkoxypyrimidines rearrange on heating to form 1,3-dialkyluracils. This method of operating makes possible the synthesis of uracil derivatives which hitherto have not been available for the development of pyrimidine chemistry.

3. A new method for the alkylation of pyrimidines of the uracil type in position **3** has been developed.

4. This new reaction will be applied for the synthesis of hexose and pentose derivatives of pyrimidines. It is possible that some of these sugar derivatives will be found to be identical with the naturally occurring nucleosides. This same technique will also be applied in the purine series.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PIPERIDINE DERIVATIVES. IX. METHYLPIPERIDINO-ALKYL CINNAMATES

BY C. F. BAILEY AND S. M. MCELVAIN

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It has been pointed out in two previous communications[1] from this Laboratory, that those piperidino-alkyl benzoates containing a methyl group as a substituent in the piperidine nucleus were much more effective as local anesthetics than the corresponding compounds in which the piperidine nucleus was unsubstituted or was substituted by certain other aliphatic groups. In two very interesting papers concerned with the correlation of aromatic properties with physiological action, Gilman and co-workers[2] have shown that in the amino-alkyl ester type of anesthetic a distinct local anesthetic effect is found associated with those structures in which the carbonyl group of the ester is attached to an unsaturated carbon atom. Of all such types of compounds that have been investigated, the cinnamates are by far the most effective. Apothesine, γ-diethylaminopropyl cinnamate, is a well-known example of this type of ester.

Since the methylpiperidino-alkyl nucleus has been found to be so efficient

[1] McElvain, THIS JOURNAL, **49**, 2835 (1927); Bailey and McElvain, *ibid.*, **52**, 1633 (1930).

[2] Gilman and co-workers, *ibid.*, **47**, 245 (1925); *ibid.*, **50**, 437 (1928).

in the benzoate series, it seemed desirable to prepare and submit for pharmacological study an analogous series of cinnamates. This paper gives the preparation, properties and a brief statement of the pharmacological action of the following six compounds: 2-methyl-, 3-methyl- and 4-methylpiperidino-ethyl and propyl cinnamates.

These substances were prepared by the condensation of the methylpiperidines'with β-chloro-ethyl cinnamate and y-chloropropyl cinnamate. The tertiary amino esters so obtained were isolated and used in the form of their hydrochlorides.

Experimental

Methylpiperidines.—The 2-methyl-, 3-methyl- and 4-methylpiperidines that were used were obtained from ***a*-**, β- and γ-picolines, respectively, by methods previously described.'

β-Chloro-ethyl Cinnamate.—This ester has previously been prepared[3] by the action of ethylene chlorohydrin on cinnamic acid in the presence of sulfuric acid. This procedure was not tried in this work since the following method gave very satisfactory results. To 111 g. of cinnamic acid in a 1-liter flask fitted with a reflux condenser, 179 g. of thionyl chloride was slowly added from a dropping funnel. The evolution of sulfur dioxide and hydrogen chloride began almost immediately. After all of the thionyl chloride had been added the mixture was heated on a steam-bath for two hours. The excess thionyl chloride was then removed by distillation. To the remaining material 61 g. of ethylene chlorohydrin was slowly added and the resulting solution heated for two hours at 180° in an oil-bath. The reaction mixture was then allowed to cool, poured into water and the immisciblelayer taken up in ether. After drying over calcium chloride the ether was removed and the remaining ester distilled under diminished pressure. There was obtained 126 g. (80% of the theoretical) of β-chloro-ethyl cinnamate which boiled at 162–163° (3 mm.). On distillation the ester crystallized in the receiver. Its melting point was found to be 35–37°. (The literature reference to this compound states that the melting point is 31°.)

Anal. (Stepanoff). Calcd. for $C_{11}H_{11}O_2Cl$: Cl, 16.86. Found: 17.03, 17.12.

γ-Chloropropyl Cinnamate.—This ester does not appear to have been described in the literature. It was prepared according to the procedure described above for β-chloro-ethyl cinnamate except that an equivalent amount of trimethylene chlorohydrin was used instead of ethylene chlorohydrin. The yield was 75% of the theoretical. The γ-chloropropyl cinnamate boiled at 174–177° (3 mm.); d_{20}^{20} 1.1512; n_D^{25} 1.5677. This ester is a liquid at ordinary temperatures.

Anal. (Stepanoff). Calcd. for $C_{12}H_{13}O_2Cl$: Cl, 15.81. Found: Cl, 15.83, 15.82.

Methylpiperidino-alkyl **Cinnamates.**—These compounds were prepared by the general procedure that was used[1] for the corresponding benzoates. There was, however, a distinct difference between the chloro-alkyl cinnamates and the chloro-alkyl benzoates in the ease with which they condensed with 2-methylpiperidine. It had been noted that the benzoates did not condense with 2-methylpiperidine to any appreciable extent under the conditions (100° for one hour) which caused quite complete condensation with 3- and 4-methylpiperidine. In the case of the chloro-alkyl cinnamates a temperature of 100" for one hour caused quite complete condensation with each of the methylpiperidines. These cinnamates were isolated as the hydrochlorides and recrys-

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[3] German Patent 239,650; *Chem. Centr.*, II, 1497 (1911).

tallized to a constant melting point from an alcohol–ether mixture. They are summarized in Table I.

TABLE I

METHYLPIPERIDINO-ALKYL CINNAMATE HYDROCHLORIDES

	Piperidino-alkyl group	M. p., °C.	Analyses. Cl, % Calcd.	Pound
1	β-2-Methylpiperidino-ethyl	178–180	11.47	11.45
2	γ-2-Methylpiperidinopropyl	179–181[a]	10 97	10.90
3	β-3-Methylpiperidino-ethyl	161–163	11 47	11.29
4	y-3-Methylpiperidinopropyl	193–196	10.97	10.90
5	β-4-Methylpiperidino-ethyl	142–145	11.47	11.39
6	γ-4-Methylpiperidinopropyl	178–181[a]	10 97	10 98

[a] The melting point of a mixture of No. 2 and No. 6 was 168–172°.

Pharmacological Report

These compounds are being studied pharmacologically by Mr. Charles L. Rose of the Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana. A preliminary report of their pharmacological properties is given in Table II. The anesthetic effect was determined by an application of a 2% solution of the anesthetic to the rabbit's cornea and noting the duration of anesthesia. Toxicities were determined by subcutaneous injection into white mice and intravenous injection into white rats. The various compounds are designated in Table II by the numbers associated with them in Table I. The analogous values for the corresponding benzoates are given in parentheses along with the cinnamate values.

TABLE II

PHARMACOLOGICAL DATA

Compound	Av. duration of anesthesia, min.	Subcutaneous toxicity to white mice, mg./kg. M.T.D.	M.L.D.	No. of mice used	Intravenous toxicity to white rats, mg./kg. M.T.D.	M.L.D.	No. of rats used
1	11 (0)	1100 (1500)	1200 (2000)	14	25 (25)	30 (30)	9
2	14 (15)	200 (800)	250 (900)	10	4 (15)	5 (17.5)	15
3	10 (0)	1700 (3000)	1800 (3500)	30	35 (25)	40 (30)	11
4	11 (11)	500 (450)	600 (500)	13	35 (20)	40 (25)	8
5	13 (11)	.. (1300)	..[a] (1400)	..	20 (40)	25 (42.5)	8
6	21 (14)	500 (....)[a]	600 (....)[a]	..	12.5 (20)	15 (22.5)	8

[a] Not determined because of scarcity of material.

Discussion of the Pharmacological Data

It is seen from the above data that, in general, the methylpiperidino-alkyl cinnamates are more active physiologically than the corresponding benzoates. This greater activity is particularly noticeable in the case of the ethyl esters, for 1 and 3 show quite marked anesthetic effect on the rabbit's cornea while the corresponding benzoates are without any such effect. The 4-methylpiperidino derivatives seem appreciably more active than the isomeric 3-methyl- and 2-methylpiperidino derivatives. With the exception of γ-3-methylpiperidinopropyl cinnamate, the toxicities of the members of the cinnamate series are, in general, greater than those of the benzoates.

Summary

1. The methylpiperidino-ethyl and propyl cinnamates have been prepared and described.

2. A comparison of their pharmacological properties with those of the corresponding benzoates is given.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

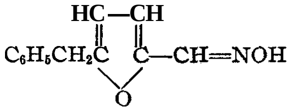
ATTEMPTED CORRELATIONS OF CONSTITUTION WITH SWEET TASTE IN THE FURAN SERIES. THE VERY HIGH SWEETENING POWER OF 5-BENZYL-2-FURFURALDOXIME

BY HENRY GILMAN AND J. B. DICKEY

RECEIVED DECEMBER 30, 1929 PUBLISHED MAY 8, 1930

Introduction

In extension of studies[1] concerned with some correlations of constitution with sweet taste in the furan series we have come upon a compound which is sweeter than saccharin. The compound is *syn*-5-benzyl-2-furfuraldoxime



and it was found to be 690 times sweeter than sugar. The anti-form of this oxime is about 100 times sweeter than sugar.

These two isomers were prepared earlier by Fenton and Robinson,[2] but apparently they overlooked the sweet taste of the compounds.

It is interesting to note that both the *syn*- and the anti-oximes of 5-hydroxymethyl-3-furfural

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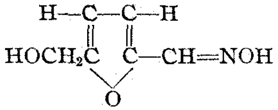
[1] (a) Gilman and Hewlett, *Iowa State Coll. J. of Sci.*, 3, 27 (1929). This article contains leading references to pertinent papers and standard texts. We omitted in that paper reference to (b) Asahina and Fujita, *J. Pharm. Soc. Japan*, 490, 1084 (1922); [*C. A.*, 17, 2578 (1923)].

[2] Fenton and Robinson, *J. Chem. Soc.*, 95, 1334 (1909).



are without sweet taste. This would hardly have been predicted. However, despite an increasing literature on taste and constitution, too little is known about the subject to warrant broad and inflexible generalizations. This is particularly true in connection with the interesting and important biological relationships of isomers, especially geometrical and optical isomers. For example, the anti-oxime of perilla aldehyde is the sweetest compound so far described, and its syn-form is without a sweet taste; the two oximes of furfural[1] appear to be equally sweet; the *syn*-oxime of furylacetaldehyde is one-half as sweet as its *anti*-isomer;[3] and our syn-oxime of 2-benzyl-furfural is about seven times sweeter than its anti-form. Of course, there is always the possibility that what is called the syn-form of some geometrical isomers may in reality be the trans form and vice *versa.*

Experimental Part

5-Chloromethyl-2-furfural, $ClCH_2(C_4H_2O)CHO$.—The 5-chloromethyl-2-furfural was prepared in accordance with the directions of Fischer and Neyman[4] from cane sugar and concd. hydrochloric acid. To prevent the emulsion described by them, the solution, after the addition of sodium carbonate, was filtered and the solid removed in this manner was washed with water to recover any chloromethyl furfural. The average yield of a number of preparations starting with 200 g. of sugar was 11.2%, and the maximum yield was 17%. The range of yield reported by Fischer and Neyman[4] was 22–25%, and the yield obtained by Middendorp[5] was 11% from one kilogram of sugar. All calculations are based on the weight of the sugar taken.

5-Hydroxymethyl-2-furfural, $HOCH_2(C_4H_2O)CHO$—Twenty-one grams (0.145 mole) of crude chloromethyl-furfural was poured into 750 cc. of boiling water and boiled for fifteen minutes. The yellowish solution containing some tar was cooled and then extracted 15 times with a total of one liter of ether until the solution was essentially colorless. The aqueous solution was salted out by saturating with hydrated sodium sulfate. The ether extract was then dried over anhydrous sodium sulfate. The yield was 45% in one experiment and 66.6% in another where the number of ether extractions was increased to 25.[6]

The two oximes of 5-hydroxymethyl-2-furfural were prepared in the manner described by Kiermayer.[7] A 62.5% yield of pure oxime was obtained from 10 g. of the crude aldehyde.

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[3] Ref. 1b. It is interesting to know, apart from furan types, that Goldschmidt, Ber., 23, 2163 (1890), reported anti-anisaldoxime as being intensely sweet, whereas the syn-form is tasteless. There is a like difference with the *p*-nitrobenzaldoximes [see Cohn, "Die Organischen Geschmacksstoffe," Berlin, **1914**].

[4] Fischer and Neyman, Ber., 47, 974 (1914).

[5] Middendorp, *Rec.* trav. *chim.*, 38, 1 (1919).

[6] When the hydrolysis was effected in boiling water containing powdered barium carbonate [Cooper and Nuttall, J. Chem. *Soc.*, 99, 1193 (1911)] there appeared to be more decomposition and the yield was 30%.

[7] Kiermayer, *Chem.-Ztg.*, 19, 1003 (1895).

5-Benzyl-2-furfuraldoxime, $C_6H_5CH_2(C_4H_2O)CH{=}NOH$.—5-Benzyl-2-furfural was prepared by the reaction of chloromethyl-furfural, benzene and aluminum chloride.[2] In addition to the two oximes which were prepared by a standard procedure,[2] we also prepared the known phenylhydrazone[2] in order further to identify our aldehyde.

Relative Sweetening Powers.—The method of evaluating the sweetness of the several oximes was that described earlier by Gilman and Hewlett.[1] The tests were carried out by a number of people.[8] By a method of cross-checking used previously by Gilman and Hewlett,[1] the currently accepted values for saccharin[9] and dulcin were first checked within the experimental error for such studies. The solutions of the sparingly soluble syn- and anti-benzyl-furfuraldoximes were made up by dissolving 0.02 and 0.04 g., respectively, of each of the oximes in 819 cc. of distilled water. The standard sugar solution (of 1.8% concentration by weight) was prepared from 0.0892 g. of sugar in 5 g. of water. The saccharin and dulcin solutions were of the same concentration as the *syn*-benzyl-furfuraldoxime.

It was found that the syn-isomer is about 690 times sweeter than sugar, and the anti-isomer about 100 times sweeter than sugar. By direct comparison it was found that the syn-isomer is slightly sweeter than saccharin. Aqueous alcoholic solutions of the oximes are decidedly sweet.

It is interesting to note that with both isomers there is an apparent lag or induction period before the sweet taste becomes apparent. This time interval between no taste and a sweet taste is very short but distinct. Once the sweet taste becomes apparent it rapidly increases to a maximum. Later the sweet taste is replaced by a pungent taste. At their respective maxima the sweet taste of the anti-form is less pleasant than that of the syn-form.

Studies are in progress on the introduction of water solubilizing groups with the hope of retaining the sweetening characteristics of the benzyl-furfuraldoximes.

The 5-hydroxymethyl-2-furfuraldoximes were devoid of sweet taste.[10]

Summary

It has been found that syn-5-benzyl-2-furfuraldoxime is sweeter than saccharin and that it is also about seven times sweeter than its *anti*-

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[8] The authors are grateful for assistance rendered by Drs. P. Mabel Nelson and Louise Jennison Peet of the Department of Foods and Nutrition; to 12 students in one of their classes in foods; and to Dr. B. W. Hammer of Dairy Bacteriology. All of these individuals have had experience in detecting and differentiating tastes in a variety of foods. In addition, we wish to thank 7 graduate students in Chemistry who helped with the several taste tests.

[9] Magidson and Gorbatschow, *Ber.*, 56, 1810 (1923). Also, Paul, *Chem.-Ztg.*, **4, 38 (1921).**

[10] Erdmann, Ber., 43,2391 (1910), reported that the corresponding hydroxymethyl-furfural has a sharp, burning taste.

isomer. Attention is directed to an apparent lack of correlation between geometrical isomers of the furan series and their sweet taste.

AMES, IOWA

[CONTRIBUTION FROM THE RESEARCH LABORATORY, THE UPJOHN COMPANY]

THE STEROLS OF ERGOT

BY MERRILL C. HART AND FREDERICK W. HEYL

RECEIVED DECEMBER 30, 1929 PUBLISHED MAY 8, 1930

In recent years considerable literature has developed about the chemistry of the ergosterol of yeast and its accompanying sterols, though but one paper[1] on the chemistry of the ergosterol of ergot since the original work by Tanret[2] has come to our attention. In this paper Rosenheim and Webster report on the irradiation of a "fungisterol" which, however, differs widely from that described by Tanret, and at the same time differs from any of the sterols accompanying the ergosterol of yeast as described by Wieland and Asano.[3]

Having at hand a considerable quantity of the ergosterol from ergot, it seemed desirable to us (1) to repeat and confirm if possible Tanret's isolation of fungisterol, and (2) to prepare a number of derivatives of our ergosterol, some previously described and some new, with a view to establishing more rigorously, or to disestablish, the complete chemical identity of the sterol from the two sources. That differences might be expected is indicated by the experience of Heilbron, Sexton and Spring,[4] who found two different specimens of ergosterol from yeast which behaved quite differently upon hydrogenation. In this paper we present our work on the fractionation of the ergot sterols; we hope in subsequent papers to report on a number of derivatives of the ergosterol of ergot.

Experimental

Preparation of **Ergosterol.**—Spanish ergot was exhaustively extracted with benzene and, after recovery of the solvent, the residue boiled with an excess of 20% alcoholic potassium hydroxide. The unsaponifiable fraction was removed in the usual way, and crude ergosterol precipitated by the addition of petroleum ether (b. p. 60–80°) to the concentrated ether extract. The yield of this crude averaged 0.13% of the ergot used. When twice crystallized from ethyl alcohol, plates melting at 152–157° were obtained. Filtration of a chloroform solution of this material removed a small amount of amorphous substance and subsequent crystallization of the soluble portion raised the melting point to 160–162°. Acetylation, crystallization of the acetate from acetic acid, ethyl and methyl alcohols, and subsequent hydrolysis, failed to raise this. $[\alpha]_D$ varied from -112.2 to $-100°$ in various runs, with the yield averaging about 60% of the crude.

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[1] Rosenheim and Webster, *Biochem. J.*, 22, 1426 (1928).

[2] Tanret, *Compt. rend.*, **108**, 98 (1889); *ibid.*, **147**, 75 (1908).

[3] Wieland and Asano, *Ann.*, **473**, 300 (1929).

[4] Heilbron, Sexton and Spring, *J. Chem. Soc.*, 926 (1929).

Crystallization from the alcohol–benzene mixture of Bills and Honeywell[5] gave in poor yield a product melting at 163–164.5° and having $[\alpha]_D$ of −123°, which is the closest we have been able to approach Tanret's values (m. p. 165°, $[\alpha]_D$ −132") by these methods. Acetylation and hydrolysis of this preparation only served to lower the melting point to 160–162° and $[\alpha]_D$ to −112°.

Separation of Fungisterol.—The combined filtrates from the purification of about 250 g. of crude ergosterol were concentrated and fractionated from ethyl acetate. A large top fraction with $[\alpha]_D$ of −64° was discarded, and the rest refractionated twice with the results shown in Table I.

TABLE I

SEPARATION OF THE FUNGISTEROL FRACTION

Fraction no.	Weight, g.	$[\alpha]_D$	M. p., °C.
1	0.3	−20.8	130–140
2	.2	−19.1	130–135
3	.2	−20.8	125–130
4	.2	−20.8	130–132
5	.2	−2.6	116–120
6	..	....	Sirup

Each of the first four fractions when recrystallized from ethyl alcohol gave a small amount of fungisterol melting at 144–146°, which yielded an acetate melting at 156–157°. Tanret gives 144° for the sterol and 158.5" for the acetate. There was not enough material to establish the elementary analysis, but it probably contains at least two more hydrogen atoms than ergosterol, since it no longer gives the Rosenheim[6] color test with trichloro-acetic acid, which is regarded as specific for the $\Delta^{1,2}$ (or $\Delta^{1,13}$) linkage in sterols. The Liebermann–Burchard test was positive, showing that fungisterol is not completely saturated. The Salkowski reaction gave in the acid layer a yellow color which reddened with extreme slowness.

Isolation of a Third Sterol.—It was evident from Table I that there was also present a third compound of even lower rotatory power than fungisterol. Fraction 5 was acetylated, yielding an acetate melting at 121–124°. Several recrystallizations from acetic anhydride and from ethyl alcohol raised this to 122–125°.

Anal. Calcd. for $C_{27}H_{45}OCOCH_3$: CH_3CO, 10.0. Found: CH_3CO, 10.0.

The sterol recovered from this hydrolysis crystallized from alcohol in plates melting at 120–125°.

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.85; H, 12.01. Found: C, 83.46; H, 11.55.

The Rosenheim color test was negative; the Liebermann–Burchard test positive; the Salkowski test gave a yellow color in the acid layer, which slowly changed to orange.

The petroleum ether filtrates from the separation of the crude ergosterol deposited on long standing considerable further crystalline material which is a mixture of the three ergot sterols. It is being worked up at present to prepare larger quantities of fungisterol and the third sterol.

Summary

1. The association of fungisterol (m. p. 144–146°, $[\alpha]_D$ −20°, acetate, m. p. 156–157°) with the ergosterol of ergot, as described by Tanret, is confirmed.

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[5] Bills and Honeywell, *J. Biol. Chem.*, *80*, 15 (1928).

[6] Rosenheim, *Biochem. J.*, 23, 47 (1929).

2. The presence of a third sterol (m. p. 120–125°, $[\alpha]_D$ −2°, acetate, m. p. 121–124°) is established.

KALAMAZOO, MICHIGAN

[CONTRIBUTION FROM THE RESEARCH LABORATORY, THE UPJOHN COMPANY]

SOME NEW ESTERS OF ERGOSTEROL

BY HAROLD EMERSON AND FREDERICK W. HEYL

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In continuation of our study of the sterols of ergot, we have prepared several new esters of ergosterol with acid derivatives which have frequently been used to characterize alcohols, namely, phthalic anhydride, phenyl isocyanate, and chloro-acetyl *o*- and *p*-nitrobenzoyl chlorides. Since it was found that the action of the acid chlorides in the absence of an agent to absorb the hydrogen chloride evolved yielded derivatives of isoergosterol, it was necessary to work in pyridine solution.

Experimental

Ergosteryl **Acid Phthalate.**—Ergosterol (2 g.) was refluxed with phthalic anhydride (3 g.) in 5 cc. of pyridine. The resulting product appeared in the form of prisms melting at 169° after several recrystallizations from alcohol; $[\alpha]_D$ was −51°.

Anal. Calcd. for $C_{35}H_{46}O_4$: C, 79.2; H, 8.7; mol. wt., 530. Found: C, 79.1; H, 8.9; mol. wt., 532 (by titration).

Upon hydrolysis with alcoholic potassium hydroxide, this gave ergosterol identical with the starting material.

The silver salt was made by adding a slight excess of an alcoholic solution of silver nitrate to the portion neutralized in titrating for the molecular weight. It separated as white crystals melting with decomposition at 170–180°, and blackening upon standing.

Anal. Calcd. for $C_{35}H_{45}O_4Ag$: Ag, 16.9. Found: Ag, 17.1.

The copper salt was prepared from cupric acetate in an analogous manner and separated as a green amorphous precipitate.

Anal. Calcd for $(C_{35}H_{45}O_4)_2Cu$: Cu, 7.06. Found: Cu, 7.17.

Ergosteryl **Phenylurethan.**—Ergosterol (1.6 g.) was refluxed with 5 cc. of phenylisocyanate and 25 cc. of benzene for three hours. The solvent and excess reagent were removed by distillation at 15 mm. and the residue was recrystallized by dissolving in hot benzene and adding alcohol to incipient precipitation. It crystallizes in short hard needles melting at 236.5–238° (corr.).

Ergosteryl m-Nitrobenzoate was prepared by refluxing 1 g. of ergosterol with 0.6 g. of *m*-nitrobenzoyl chloride in 5 cc. of pyridine for one hour. The reaction mixture was poured into hot alcohol and allowed to crystallize. It was purified by recrystallization from alcohol, forming tiny plates melting at 151°; $[\alpha]_D$ was −71°.

Ergosteryl **_p_-Nitrobenzoate** was made in a similar manner. It formed clusters of plates melting at 182°; $[\alpha]_D$ was −49.5°. Both this and the meta compound yielded ergosterol upon hydrolysis.

The m- and *p*-nitrobenzoates of isoergosterol were formed by melting together ergosterol and the corresponding acid chloride either in toluene or without a solvent. Upon crystallization from alcohol they melted at 172° (m-) and 189° (*p*-), respectively, and were both optically inactive.

Anal. Calcd. for $C_{34}H_{45}O_4N$: C, **76.8;** H, **8.5.** Found: (meta) C, **76.6;** H, **8.9;** (para) C, **76.5;** H, 8.9.

When hydrolyzed, both yielded isoergosterol, as plates melting at 137° with $[\alpha]_D$ of -32.6". Bills and Cox[1] give m. p. 140°, $[\alpha]_D$ $(= [\alpha]_{5461} \div 1.27) = -31.2°$ for isoergosterol made by treatment with cinnamoyl chloride.

Chloro-acetyl Derivatives.—An attempt was made to prepare ergosteryl chloro-acetate by warming ergosterol with the acid chloride in pyridine, but this resulted in a halogen-free compound, due to a further condensing effect of the pyridine. The nature of this reaction will be reported in a later paper.

Isoergosteryl chloro-acetate was readily obtained by warming **1.7** g. of ergosterol with **2** cc. of chloro-acetyl chloride on a steam-bath for three minutes. Crystallized from acetic acid and from ether it gave **1.2** g. of plates melting at 190°; $[\alpha]_D$ was $-45°$.

Anal. Calcd. for $C_{29}H_{43}O_2Cl$: Cl, **7.7.** Found: Cl, **8.0.**

Hydrolysis gave the same isoergosterol described above

Summary

Ergosteryl acid phthalate and its silver and copper salts, ergosteryl phenylurethan and *m*- and *p*-nitrobenzoates have been prepared from the ergosterol of ergot, as well as the *m*- and *p*-nitrobenzoates and chloro-acetate of isoergosterol.

KALAMAZOO, MICHIGAN

[CONTRIBUTION FROM THE RESEARCH LABORATORY, THE UPJOHN COMPANY]

ALPHA-ERGOSTENOL AND ITS ISOMERIZATION TO BETA-ERGOSTENOL

BY MERRILL C. HART, JOHN H. SPEER AND FREDERICK W. HEYL

RECEIVED DECEMBER 30, 1929 PUBLISHED MAY 8, 1930

Since ergosterol itself and its esters, containing as they do three double bonds, are decidedly unstable and acquire a distinct yellow color on standing even in a black vacuum desiccator, we decided to continue our investigation of the ergosterol from ergot by studying its very stable tetrahydro derivatives, a- and β-ergostenol. α-Ergostenol was first prepared by Reindel and co-workers[1] from yeast ergosterol by catalytically reducing the acetate and hydrolyzing the product obtained thereby. The same compound has later been prepared by other authors with variations of the catalyst and solvents used. α-Ergostenol as we have prepared it from ergot ergosterol differs slightly in physical constants from Reindel's values, and did not react at all to his method of isomerization to the β-form (passing dry hydrogen chloride gas into a chloroform solution of a-ergostenol acetate). The statement of Reindel, Walter and Rauch that "the chloro-acetyl derivative of a-ergostenol cannot be made by chloro-acetyl chloride, since thereby isomerization to β-ergostenol chloro-acetate takes place"

[1] Bills and Cox, J. *Biol. Chem.*, **84,455 (1929).**

[1] Reindel, Walter and Rauch, ***Ann.*, 452, 34 (1927);** Reindel and Walter, *ibid.*, **460, 212 (1928).**

led us to attempt the preparation of β-ergostenol acetate by esterification with acetyl chloride, instead of the anhydride which is normally used to form acetates without danger of isomerization. The fact that this yielded an acetate identical in every respect with genuine α-ergostenol acetate made it seem of interest to investigate the effect of a number of acid chlorides in causing this isomerization.

Experimental

Preparation of α-Ergostenol.—Three grams of ergosterol acetate (m. p. 170–172°, $[\alpha]_D$ −74.5°) was shaken with 0.3 g. of Adams[2] platinum oxide catalyst and 300 cc. of glacial acetic acid with 2 atmospheres of hydrogen at room temperature. The acetate rapidly dissolved, and the absorption of two mols of hydrogen was complete in about fifteen minutes Continued shaking and fresh catalyst did not cause any further absorption. After filtration from the catalyst and concentration of the solution, α-ergostenol acetate separated as plates melting at 110–111^e which were optically inactive. Reindel and co-workers give $[\alpha]_D$ +5.18°; yield, almost quantitative.

Sixty grams of this material was systematically fractionally crystallized from acetic acid five times, with the results shown in Table I.

TABLE I

FRACTIONATION OF α-ERGOSTENOL ACETATE

Fraction no.	Weight, g.	M. p., °C.	$[\alpha]_D$
1	11.83	110–111	0
2	8.00	110–111	0
3	14.08	109–110	0
4	11.10	109–110	0
6	5 24	107–108	0
6	2.07	103–106	0

Fractions 1–4 gave on hydrolysis a-ergostenol melting sharply at 133° and having $[\alpha]_D$ +10.5°. Reindel and co-workers give m. p. 130–131"; $[\alpha]_D$ +17.86°. This discrepancy is most simply explained by the difference in source of the ergosterol.

α-Ergostenol was quantitatively precipitated by digitonin, and was recovered unchanged by decomposing the digitoinide with boiling xylene.

Treated in chloroform solution with dry hydrogen chloride gas according to Reindel's directions, a-ergostenol acetate was consistently recovered unchanged in better than 80% yields, although Reindel reports yields of 95% of β-ergostenol acetate. As noted in the introduction, an attempt to prepare p-ergostenol acetate by the action of acetyl chloride on a-ergostenol also failed. We could without difficulty, however, prepare the p-ergostenol chloro-acetate, m. p. 166–167° reported by Reindel, by the action of chloro-acetyl chloride on or-ergostenol. We also confirmed their observation of a "back-isomerization" upon hydrolysis, since we obtained not pure β-ergostenol but a mixture containing some α-ergostenol, from which it was impossible to separate the pure β-form by fractional crystallization.

In order to determine if possible the conditions for isomerization, we prepared *a* series of esters as shown in Table II by warming 0.5 g. of α-ergostenol with 0.5 g. of acid halide and recrystallizing from alcohol. Hydrolysis with alcoholic potassium hydroxide gave either the characteristic low melting mixture of a- and p-ergostenol, or the homo-

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[2] Voorhees and Adams, THIS JOURNAL, 44, 1397 (1922); Adams and Shriner, *ibid.*, 45,2171 (1923).

geneous sharp melting needles of α-ergostenol, according as isomerization had or had not taken place. As a control experiment, esterification was also carried out in pyridine solution,[3] resulting in every case in an a-ergostenol derivative as shown in Table III. (Compounds which were identical with those in Table II are omitted from Table III.)

TABLE II

ESTERIFICATION OP α-ERGOSTENOL WITHOUT SOLVENT

Ester	M. p., °C.	Analysis, % Calcd.	Analysis, % Found	M. p. of hydrolysate
Acetate	110–11			131
Monochloro-acetate	166–67	Cl, 7.69	7.71	110–12
Dichloro-acetate	114	Cl, 14.27	13.48	132
Trichloro-acetate	128	Cl, 20.01	19.66	108–11
Propionate	114–15	C, 81.36, H, 11.18	81.53, 11.02	108–12
a-Bromopropionate	104.5	Br, 15.34	15 47	112–14
Butyrate	74–75	C, 81.49, H, 11.50	81.56, 11 22	110–11
Benzoate	117.5[a]	C, 83.17, H, 10.29	82.96, 10.19	130–31
m-Nitrobenzoate	165	N, 2.61	2.38	132
p-Nitrobenzoate	178	N, 2.61	2.66	132

[a] Reindel, Walter and Rauch give 118° for α-ergostenol benzoate.

TABLE III

ESTERIFICATION OR α-ERGOSTENOL WITH PYRIDINE AS SOLVENT

Ester	M. p., °C.	M. p. of hydrolysate, °C.
Monochloro-acetate	[a]	130–131
Trichloro-acetate	133.5	129–131
Propionate	90	129–130
a-Bromopropionate		130–131
Butyrate	67–68	130–131

[a] These two compounds were not true esters of α-ergostenol, a further reaction due to the condensing effect of the pyridine having taken place. Their true nature is being investigated.

It is difficult to understand why some acid halides should cause isomerization while others do not. It cannot be explained on the basis of the "strength" of the acid involved, for acetic acid stands intermediate between butyric and the chloro-acetic acids, and dichloro-acetic acid between monochloro- and trichloro-acetic acids in strength. Likewise, the presence or absence of halogen in the acid chain cannot be made to account for the results. In every case a copious evolution of hydrogen chloride was observed, so the presence of dry hydrogen chloride alone is not sufficient to effect isomerization. We are forced to the conclusion that the reaction is one the course of which cannot be predicted with our present knowledge.

Summary

1. a-Ergostenol prepared from ergot ergosterol was found to differ slightly in physical properties, and radically in ability to isomerize, from

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[3] Houben, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, 1925, Vol. II, 3d ed., p. 667.

the a-ergostenol from yeast ergosterol as described by Reindel, Walter and Rauch.

2. The effect of a number of acid halides in causing isomerization of a-ergostenol to β-ergostenol has been investigated; no single factor could be made to account for isomerization in some cases and not in others.

3. A number of new esters of α- and of β-ergostenol are described.

KALAMAZOO, MICHIGAN

[CONTRIBUTION FROM THE DERMATOLOGICAL RESEARCH LABORATORIES]

AROMATIC AMIDES OF N-ARYLGLYCINE ARSONIC ACIDS

BY GEORGE W. RAIZISS AND LE ROY W. CLEMENCE

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In the search for therapeutic arsenical compounds, used in the treatment of syphilis, Jacobs and Heidelberger[1] deviated from the usual experimental lines, which involved changes in the aromatic nucleus containing arsenic. These older researches had involved changes in the structure of salvarsan base (diamino-di-hydroxy-arsenobenzene) and this field of study has been fairly well exhausted.

The above authors synthesized a new series of compounds utilizing the reaction between chloro-acetyl-alkyl or chloro-acetyl-aryl amines and arsanilic acid (*p*-aminophenylarsonic acid). The aromatic series furnished a new field for work inasmuch as the non-arsenical benzene nucleus could be still further substituted, giving rise to compounds of substituted chloro-acetyl-aryl amines and arsanilic acid. A large number of such compounds were prepared.

It is our purpose to add further to this series and in doing so we have used the chloro-acetyl derivatives of amines which in themselves are therapeutic to some degree. We have also obtained some compounds involving 3-methylarsanilic acid (*m*-methyl-*p*-amino-arsonic acid) which correspond to the known derivatives of arsanilic acid.

The intermediate compounds used by us in the preparation of the arsonic acids are chloro-acetyl derivatives of amines. In most of the experiments these were prepared by methods employed by Jacobs and Heidelberger;[2] the few exceptions will be described later.

Jacobs and Heidelberger in their experiments[3] employed arsanilic acid, and its corresponding derivatives, in the form of its sodium salt (*i. e.*, in alkaline solution). For several of our experiments this was not practicable inasmuch as the chloro-acetyl compounds were oxidizable in alka-

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[1] Jacobs and Heidelberger, THIS JOURNAL, 41, 1581 (1919).

[2] Jacobs and Heidelberger, *ibid.*, 39, 1439 (1917); 41, 458 (1919); J. *Biol. Chem.*, 20, 686 (1915).

[3] Jacobs and Heidelberger, THIS JOURNAL, 41, 1587 (1919).

line mediums and gave very dark colored products, this being especially the case with 5-chloro-acetylaminosalicylic acid.

In such cases we employed the free arsanilic acid (or derivative) in aqueous medium. This required more time for the reaction and in a few instances reduced the yield; nevertheless the product was purer in composition and much lighter in color. Then, again, according to Jacobs and Heidelberger,[4] the reaction between arsanilic acid and chloro-acetylanthranilic acid did not go in the desired sense entirely, due to the high reactivity of the chlorine atom in the chloro-acetyl compound, resulting in side reactions and an impure product. We considered that this was perhaps due to the presence of sodium hydroxide, so we employed only a water medium. The product we obtained showed by analysis that it was not exactly pure, but still it was practically so, and on further purification would finally have yielded an absolutely pure product.

All of the arsonic acids we prepared are crystalline products with the possible exception of the N-(phenyl-4-arsonic acid)-glycyl-acriflavine, which is a very fine amorphous powder.

The subsequently mentioned compounds were elaborated with a view to possible application in the treatment of syphilis. The major requirements for qualification of a chemical substance as a therapeutic agent are therapeutic efficiency and relatively low toxicity, allowing a large margin of safety between the therapeutic and the toxic doses. From the point of view of toxicity some of our preparations showed remarkably high qualities. When injected into rabbits they proved to be of much lower toxicity than other pentavalent arsenicals, including tryparsamide and stovarsol (acetarsone), both accepted antisyphilitic drugs and generally considered of low toxicity.

TOXICITY OF VARIOUS ORGANIC COMPOUNDS OF ARSENIC WHEN ADMINISTERED INTRAVENOUSLY TO RABBITS

Compound	Max. tolerated dose calcd. per kg. of body weight, g.	Lethal dose, g.
Arsanilic acid	0.08	0.1
Tryparsamide (sodium N-phenylglycine-amide-p-arsonic acid)	1	1.25
Stovarsol (3-acetyl-amino-4-hydroxyphenylarsonic acid)	0.1	0.12
Sodium salt of stovarsol	0.5	0.6
Arsonodiacetyl-(diacetyl-3,5-diamino-4-hydroxy-phenyl-arsonic acid)	0.8	1
N-(phenyl-4-arsonic acid)-glycyl-5'-amino-salicylic acid	0.9	1
N-(phenyl-4-arsonic acid)-glycyl-5'-amino-salicylic acid (sodium salt)	1.75	2
N-(phenyl-2-methyl-4-arsonic acid)-glycyl-5'-amino-salicylic acid	0.9	1

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[4] Jacobs and Heidelberger, THIS JOURNAL, 41, 1627 (1919).

Thus, N-(phenyl-4-arsonic acid)-glycyl-5′-aminosalicylic acid (sodium salt) is considerably less toxic for rabbits than tryparsamide and the sodium salt of stovarsol. The results of the spirocheticidal tests of this compound, however, were not very encouraging.

RESULTS OF INTRAVENOUS INJECTIONS OF N-(PHENYL-4-ARSONIC ACID)-GLYCYL-5′-AMINO-SALICYLIC ACID INTO RABBITS INOCULATED WITH TREPONEMA PALLIDUM

Dose per kilo of body weight, g.	Dark field negative for spirochetes after	Testicles normal after	Testicles remained normal (last examination)	Results of lymph node transplantation into control animals
0.15	14 days	Animal died after 3 days		
0.15	26 days	61 days	116 days	Negative
0.3	9 days	48 days	70 days	Negative

While this compound, as seen from the above table, is capable of destroying spirochetes in the animal body, it is evident that a dose had to be employed which was quite near to the maximum tolerated, in order to obtain early negative results in the dark field examination. It took nine days to make spirochetes disappear from lesions when the dose of 0.3 g. was used, *i. e.*, one-third of the maximum tolerated dose. For comparison, it was found by us that only 0.015 g. (about one-eighth of the maximum tolerated dose) of arsphenamine was required to obtain the same result in one day.

The same compound did not prove to be of therapeutic value in experimental trypanosomiasis in albino rats when injected intravenously in the dose of 1.1 g. per kilo (rats tolerated it in as high a dose as 4.5 g.).

Experimental Part

Preparation of **Chloro-acetyl Amines.**—The general method for chloro-acetylation is as follows: 1 mole of the amino compound or hydrochloride is dissolved or suspended in 1 liter of ice and water and cooled in a bath of ice water. Then with good stirring 1.5–2 moles of chloro-acetyl chloride is slowly added. The chloro-acetyl compound separates and is filtered. It is then washed with water or 2% hydrochloric acid, except in the cases of chloro-acetylamino-antipyrine and chloro-acetylacriflavine, which are both somewhat soluble in water. With the exception of these two compounds, all can be recrystallized from water.

TABLE I

CHLORO-ACETYL COMPOUNDS

( )-Chloro-acetyl	Formula	M. p., °C.	Nitrogen, % Calcd.	Found
4-( )-aminobenzoic acid	*p*-$(CH_2ClCO)NHC_6H_4COOH$	248	6.56	6.55
2-( )-(4-nitro)-toluidine	$ClCH_2CONHC_6H_3(NO_2)CH_3$-(*p,o*)	151	12.25	12.08
5-( )-aminosalicylic acid	$ClCH_2CONHC_6H_3(OH)COOH$-(*p,o*)	242–244	6.10	6.19
( )-amino-antipyrine	$ClCH_2CONHC_{11}H_{11}N_2O$	187	Cl, 12.66	12.87
( )-acriflavine	$ClCH_2CONHC_{14}H_{12}N_2Cl$	215–220, d.	......	...
4-( )-aminoguaiacol	$ClCH_2CONHC_6H_3(OCH_3)OH$-(*m,p*)	117	6.48	6.29

Preparation of Arsonic Acid **Amides** in Alkaline Medium.—The method used was that of Jacobs and Heidelberger in which the arsonic acid is dissolved in alkali to give the sodium salt in solution, except that we used 2 moles of the arsonic acid instead of 1 mole.

Two moles of arsanilic acid (or 3-methylarsanilic acid) was dissolved in a volume of normal sodium hydroxide solution (2 moles) and to this was added 1 mole of the chloro-acetyl amine. The mixture was then heated under a reflux condenserfor a time, varying with each reaction. Usually after refluxing for one to two hours the solid matter goes into solution, and on further heating precipitates again. In some cases the solid matter never goes into solution. The reaction is usually finished when a test portion of the mixture is completely soluble in alkali. The mixture is then made acid to congo red with hydrochloric acid and filtered off. The crude arsonic acid amide is insoluble. This can be purified by washing well with dilute hydrochloric acid and water, then dissolving in dilute sodium hydroxide, treating with "nuchar" and reprecipitating with hydrochloric acid while hot. The purified amides are insoluble in hot or cold water, insoluble in organic solvents, insoluble in dilute acids but soluble in dilute alkali. The following amides were prepared in this manner.

TABLE II

ARSONIC ACID AMIDES FROM ALKALINE MEDIUM

Compound	M. p., °C.	Time of reaction, hours
N-(Phenyl-4-arsonic acid)-glycyl-4'-aminobenzoic acid	Darkens at 230, melts at 260–265 (dec.)	3
N-(Phenyl-2-methyl-4-arsonic acid)-glycine-2'-toluidide	246 (dec.)	5
N-(Phenyl-4-arsonic acid)-glycine-(4'-nitro)-o-toluidide	115–120 (dec.)	6
N-(Phenyl-4-arsonic acid)-glycyl-amino-antipyrine	270 (dec.)	6
N-(Phenyl-4-arsonic acid)-glycyl-4'-aminoguaiacol	215–217	5

Formula	Nitrogen, %		Arsenic, %	
	Calcd.	Found	Calcd.	Found
p-$H_2O_3AsC_6H_4NHCH_2CONHC_6H_4COOH$-*p*	7.08	6.90	19.00	18.55
o,p-$CH_3(H_2O_3As)C_6H_3NHCH_2CONHC_6H_4CH_3$-*o*	7.36	6.93	19.80	20.01
p-$H_2O_3AsC_6H_4NHCH_2CONHC_6H_3(NO_2)CH_3$-*p,o*	10.24	10.04	18.35	17.86
p-$H_2O_3AsC_6H_4NHCH_2CONHC_{11}H_{11}N_2O$	..	..	16.24	15.90
p-$H_2O_3AsC_6H_4NHCH_2CONHC_6H_3(OCH_3)OH$-*m,p*	7.07	6.82	18.93	19.19

Preparation of **Arsonic** Acid **Amides** in Aqueous Medium.—This method is practically the same as the previous one with the omission of the alkali. The reactions require longer heating but the yields are approximately equal to those in reactions employing sodium hydroxide. The yields in both cases range from 25–40% based on the chloro-acetyl compound.

TABLE III

ARSONIC ACID AMIDES FROM AQUEOUS MEDIUM

Compound	M. p., °C.	Time of reaction, hours
N-(Phenyl-2-methyl-4-arsonic acid)-glycyl-4'-aminobenzoic acid	Dec.	3
N-(Phenyl-2-methyl-4-arsonic acid)-glycine-anilide	>275	6.
N-(Phenyl-2-methyl-4-arsonic acid)-glycine-(4'-nitro)-o'-toluidide	285–286 (dec.)	10
N-(Phenyl-2-methyl-4-arsonic acid)-glycine-p'-amino-acetanilide	......	40

TABLE III (Concluded)

Compound	M. p., °C.	Time of reaction, hours
N-(Phenyl-4-arsonic acid)-glycyl-5′-aminosalicylic acid	Darkens at 190, melts at 230–235 (dec.)	8
N-(Phenyl-2-methyl-4-arsonic acid)-glycyl-5'-aminosalicylic acid	240–245 (dec.)	10
N-(Phenyl-4-arsonic acid)-glycyl-acriflavine	Darkens at 240, does not melt below 300	6
N-(Phenyl-2-methyl-4-aesonic acid)-glycine-β′-naphthylamide	260–262 (dec.)	8
N-(Phenyl-2-methyl-4-arsonic acid)-glycine-a'-naphthylamide	254–255 (dec.)	8
N-(Phenyl-2-methyl-4-arsonic acid)-glycine-piperidide	......	12
N-(Phenyl-2-methyl-4-arsonic acid)-glycine-benzylamide	>275	15
N-(Phenyl-2-methyl-4-arsonic acid)-glycyl-anthranilic acid	......	6

Formula	Nitrogen, %		Arsenic, %	
	Calcd.	Found	Calcd.	Found
o,p-$CH_3(H_2O_3As)C_6H_3NHCH_2CONHC_6H_4COOH$-$p$	6 84	6.34	18.33	18.10
o,p-$CH_3(H_2O_3As)C_6H_3NHCH_2CONHC_6H_5$	7 67	7.64	20.54	20.87
o,p-$CH_3(H_2O_3As)C_6H_3NHCH_2CONHC_6H_3(NO_2)CH_3$-$p,o$	9 90	9.52	17.68	17.20
o,p-$CH_3(H_2O_3As)C_6H_3NHCH_2CONHC_6H_4NHCOCH_3$-$p$	9.95	9.52	17.77	18.04
p-$H_2O_3AsC_6H_4NHCH_2CONHC_6H_3(OH)COOH$-$p,m$	6 83	6 55	18.29	18.05
o,p-$CH_3(H_2O_3As)C_6H_3NHCH_2CONHC_6H_3(OH)COOH$-$p,m$	6 09	6 04	16.54	16.14
p-$H_2O_3AsC_6H_4NHCH_2CONHC_{14}H_{12}N_2Cl$	..	..	10.83	10.72
o,p-$CH_3(H_2O_3As)C_6H_3NHCH_2CONHC_{10}H_7$-$\beta$-	6 74	6.43	18.07	18.48
o,p-$CH_3(H_2O_3As)C_6H_3NHCH_2CONHC_{10}H_7$-$\alpha$-	6.74	6.37	18.07	18.45
o,p-$CH_3(H_2O_3As)C_6H_3NHCH_2CONC_5H_{10}$	..	..	21.00	21.33
o,p-$CH_3(H_2O_3As)C_6H_3NHCH_2CONHCH_2C_6H_5$	7.38	7.13	19.78	20.10
o,p-$CH_3(H_2O_3As)C_6H_3NHCH_2CONHC_6H_4COOH$-$o$	6.84	6.37	18.33	17.82

Two moles of arsanilic acid (or 3-methylarsanilic acid) is suspended in one liter of water and 1 mole of chloro-acetylamino compound added. The mixture is then heated until a test portion shows complete solubility in alkali. In some of the reactions the insoluble matter does not go completely into solution and the reaction is very slow, requiring long heating, as is particularly the case with *p*-chloro-acetylamino-acetanilide, which is heated for forty hours. After acidification with hydrochloric acid, the product is filtered and washed. It is purified by using "nuchar" and reprecipitating from alkaline solution. The amides obtained by this method are also insoluble in all solvents except dilute alkali.

Summary

1. Some new arsonic acids have been prepared following the work of Jacobs and Heidelberger.

2. The preparation of intermediate chloro-acetyl compounds has been described.

3. Some of the preparations described proved to be valuable, being of low toxicity. Their therapeutic effect, however, was found to be low.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OP PHARMACOLOGY, SCHOOL OP MEDICINE, WESTERN RESERVE UNIVERSITY]

CONDENSATION PRODUCTS OF AROMATIC ALDEHYDES WITH A,-ANGELICA LACTONE[1]

BY W. F. VON OETTINGEN

RECEIVED JANUARY 3, 1930 PUBLISHED MAY 8, 1930

J. Thiele, R. Tischbein and E. Lossow[2] described the condensation of anisaldehyde and Δ_2-angelica lactone with the formation of a-anisal-Δ_2-angelica lactone. In a study on the relation between chemical constitution and pharmacological action concerning the anthelmintic properties of some aliphatic lactones,[3] it was found that both the Δ_2- and Δ_1-angelica lactone produce a very marked depression of the musculature and to a smaller extent also of the nervous system, but these compounds could not be utilized as anthelmintics on account of their chemical instability and general toxicity. Eugenol is also a muscular depressant and is used as an anthelmintic; its action is said to depend upon the position of the OH and OCH_3 of the ring. Therefore, it appeared to be feasible to combine both the eugenol and the angelica lactone by condensing vanillin with Δ_2-angelica lactone by the method used by Thiele and his co-workers. Because this condensation was successful, a series of similar compounds was synthesized, in order to study the relation between chemical constitution and pharmacological action of these compounds.

It would have been logical to start with the a-benzal-Δ_2-angelica lactone, *i.* e., the angelica lactone in which the Hz group is substituted by a benzyl ring, but Thiele had already found that the compound is very unstable, the lactone ring being split with the formation of benzal-levulinic acid. In the present study it was also found impossible to obtain a pure product. The same holds true for the a-phenol acetal, the a-cinnamal- and the α-hydrocinnamal-Δ_2-angelica lactones.

On the other hand, it was found possible to prepare and to isolate the corresponding derivatives of the salicyl- and resorcylaldehyde in crystalline form.

Because it is known that closure of the phenol group reduces the pharmacological action of phenols, three further compounds were prepared, in which one or two hydroxy groups were masked by methyl groups. The compounds are a-anisal-, a-vanillal- and α-piperonal-Δ_2-angelica lactone.

The Δ_2-angelica lactone was prepared according to the directions of R. Gilmour,[4] which gave very satisfactory results.

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[1] This investigation has been made with the assistance of a grant from the Committee on Therapeutic Research, Council on Pharmacy and Chemistry, American Medical Association.

[2] J. Thiele, R. Tischbein and E. Lossow, ***Ann.,*** 319, 180 (1901).

[3] W. F. von Oettingen, *J. Pharm. Exptl. Therapy,* 36, 335 (1929).

[4] R. Gilmour, *J. Chem. Soc.,* **105,** 75 (1914).

The condensation of the aromatic aldehydes with the Δ_2-angelica lactone was accomplished by heating small quantities of the angelica lactone, usually 2 *g.*, with little more than the equimolecular quantity of the aldehyde on the water-bath for a half to one hour with the occasional addition of a few drops of diethylamine. The condensation product was then shaken with sodium bisulfite solution (20 cc. of 15% solution), in order to remove the excess aldehyde; the resulting resinous mass was then dissolved in methyl alcohol, crystallized and recrystallized. Elementary analyses of the compound were made by Professor N. A. Lange of Case School of Applied Science. A study of the pharmacological action of these compounds will appear at another place; Table I gives the properties of the compounds thus obtained.

TABLE I

CHEMICAL PROPERTIES OF THE AROMATIC–ALIPHATIC LACTONES

	α-( )-Δ_2-Angelica lactones				
Property	Salicylal	Resorcylal	Anisal	Vanillal	Piperonal
M. p. °C.	96	167–168	99	143	125
Soly., water	1/2000	1/10000	1/50000	1/50000	1/50000
Soly., N saline	1/2000	1/10000	1/50000	<1/50000	<1/50000
Soly., alcohol	Fairly	Fairly[a]	Fairly	Fairly	Fairly
Soly., ether	Slightly	Slightly	Fairly	Slightly	Fairly
Soly., chloroform	Freely	Freely	Freely	Freely	Freely
Soly., benzene	Fairly	Slightly	Freely	Slightly	Freely
Soly., olive oil	Fairly	Slightly	Fairly	Fairly	Fairly
Molecular wt.	202	218	216	232	230
Formula	$C_{12}H_{10}O_3$	$C_{12}H_{10}O_4$	$C_{13}H_{12}O_3$	$C_{13}H_{12}O_4$	$C_{13}H_{10}O_4$
C, calculated, %	71.25	66.02	72.19	67.21	67.80
C, found, %	71.67	65.85	72.2	66.78	67.61
H, calculated, %	4.99	4.62	5.6	5.21	4.38
H, found, %	5.01	4 54	5.51	5.19	4.20

[a] Shows blue fluorescence in alcoholic solution.

Summary

A series of aromatic aliphatic lactones has been synthesized, namely, a-salicylal-Δ_2-angelica lactone, α-resorcylal-Δ_2-angelica lactone, α-anisal-Δ_2-angelica lactone, a-vanillal-Δ_2-angelica lactone and a-piperonal-Δ_2-angelica lactone. The chemical properties are described.

CLEVELAND, OHIO

[Contribution from the Chemical Laboratory of the University of Colorado]

THE ACTION OF GUANIDINE CARBONATE AND OF BENZAMIDINE HYDROCHLORIDE UPON GLYOXAL SODIUM BISULFITE

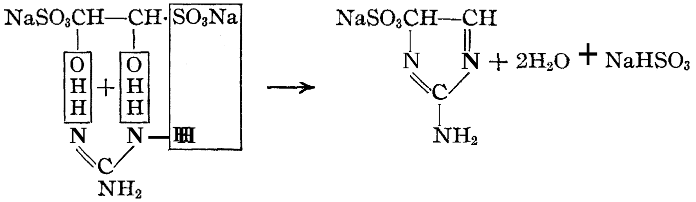
By John B. Ekeley and Jervis M. Fulmer

Received January 7, 1930 Published May 8, 1930

Very little has been published upon the reaction of guanidine or of benzamidine salts upon dialdehydes and diketones and, so far as we know, nothing upon their reactions with glyoxal sodium bisulfite. Wense[1] obtained mono- and diguanylbenzil and diguanylphenanthrenequinone from guanidine carbonate with benzil and phenanthrenequinone, respectively. By the action of benzamidine hydrochloride upon diacetyl, Diels and Schleich[2] obtained a very interesting addition product which, from its properties, seems to be a dihydroglyoxaline derivative.

This paper will describe compounds obtained by condensing guanidine carbonate and benzamidine hydrochloride, respectively, with glyoxal sodium bisulfite.

Guanidine carbonate reacts with glyoxal sodium bisulfite yielding the sodium salt of an aminosulfonic acid of a tautomeric form of glyoxaline, according to the following reaction



That the compound has the structure assigned to it is shown by the analysis, by the absence of a NH group (Liebermann's reaction), and by the fact that the NH_2 group may be replaced by OH by treatment with nitrous acid, yielding the corresponding hydroxy acid. Acidifying the salt or carrying out the reaction in acid solution would be expected to give the free acid. This, however, is not the case, since, as fast as the acid group is liberated, it reacts with the amino group, yielding the inner salt A, as is shown by the fact that the resulting compound is neutral. Boiling this compound with sodium hydroxide yields the original sodium salt. Nitrous acid reacts with the inner ammonium salt giving the corresponding hydroxy acid, B.

Benzamidine hydrochloride reacts in a similar manner with glyoxal sodium bisulfite, in this case forming the sulfonic acid of a tautomeric form of phenylglyoxaline, C.

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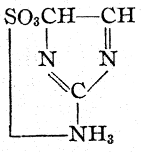
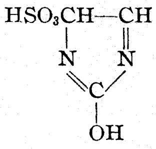
[1] Wense, *Ber.*, 19,762 (1886).

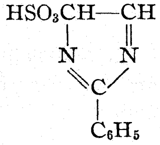
[2] Diels and Scheich, *ibid.*, 49,1713 (1916).



A



B



C

At 100° the compound, if slightly impure, loses sulfur dioxide and water, changing to a dark red resinous solid. Even at 80° the decomposition takes place slowly and at the end of a week the sample lost 26.3% of its weight. After raising the temperature to 100°, it lost 33.8%. The theoretical loss for sulfur dioxide in the above compound is 26.45% and for sulfur dioxide and water is 33.9%. If the compound is pure, it is stable, the crystals remaining unchanged apparently indefinitely.

Experimental

Sodium Salt of 2,4-Aminoglyoxalinesulfonic Acid.—Guanidine carbonate and glyoxal sodium bisulfite were brought together in water solution and boiled. Carbon dioxide was given off and, on evaporating the solution, colorless crystals were obtained. There was some decomposition during the concentration, the solution becoming light brown. The crystals were recrystallized from hot water, yielding colorless transparent prisms, which on drying became opaque. The sample for analysis was dried at 100° and melted at 260–263°.

Anal. Calcd. for $C_3H_4N_3NaSO_3$: C, 19.44; H, 2.18; N, 22.70; S, 17.32; Na, 12.42. Found: C, 19.22; H, 2.20; N, 22.41; S, 17.68; Na, 12.51.

The mother liquor was evaporated and allowed to cool, whereupon crystals of acid sodium sulfite separated out.

Inner Ammonium Salt of Aminoglyoxalinesulfonic Acid.—This compound is formed when the above sodium salt is acidified with hydrochloric acid or when water solutions of equimolecular proportions of guanidine carbonate and glyoxal sodium bisulfite are mixed, acidified with hydrochloric acid, concentrated and allowed to crystallize, whereupon colorless crystals of the inner salt are obtained. Recrystallized from hot water, they melt at 172–174°.

Anal. Calcd. for $C_3H_4N_3SO_3H$: C, 23.36; H, 2.61; N, 27.27; S, 20.80. Found: C, 23.33; H, 3.01; N, 27.02; S, 21.11.

2-Hydroxy-4-glyoxalinesulfonic Acid.—To an ice-cold water solution of the inner ammonium salt, acid with hydrochloric acid, cold sodium nitrite solution was added and allowed to stand. On concentrating the solution, colorless crystals were obtained which, recrystallized from hot water, melted at 225°.

Anal. Calcd. for $C_3H_3N_2SO_4H$: N, 17.07. Found: N, 17.10.

2-Phenyl-4-glyoxalinesulfonic Acid.—Molecular quantities of benzamidine hydrochloride and glyoxal sodium bisulfite were dissolved in warm water, mixed and concentrated on the water-bath. On cooling, a colorless crystalline compound was obtained which, recrystallized from hot water, melted at 109°. When impure, the crystals gradually decompose, but the pure compound is stable.

Anal. Calcd. for $C_9H_7N_2SO_3H$: C, 44.62; H, 4.13; N, 11.57; S, 13.22. Found: C, 44.74; H, 4.06; N, 11.53; S, 13.08.

Summary

1. The inner ammonium salt of 2-amino-4-glyoxalinesulfonic acid has been prepared. On boiling with sodium hydroxide, the sodium salt of the acid is obtained.
2. 2-Hydroxy-4-glyoxalinesulfonic acid has been prepared.
3. 2-Phenyl-4-glyoxalinesulfonic acid has been prepared.

BOULDER, COLORADO

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

NORMAL VALEROLACTONE. II. ITS VAPOR PRESSURE

BY H. A. SCHUETTE AND RALPH W. THOMAS

RECEIVED JANUARY 10, 1930 PUBLISHED MAY 8, 1930

During the course of a study of the chemical and physical properties of n-valerolactone under way in this Laboratory, it became desirable to verify the statement that this compound distils without decomposition[1] at 206–207°. A determination of its vapor pressure, which hitherto has not been reported, seemed to afford the most direct method of approach in the attack on this problem.

Experimental Procedure

The n-valerolactone used in this study was prepared by the reduction of levulinic acid as described by one of us.[2] That which was used for experimentation was dried over anhydrous sodium sulfate and redistilled, the fraction boiling at 125.3 ± 0.2° (68 mm.) serving for the vapor pressure measurements.

Vapor pressure measurements were made over the temperature range 69 to 203.4° by the dynamic method of Ramsay and Young[3] and the static method described by Smith and Menzies.[4] In both methods pressures were read directly from a manometer with the aid of lenses. They are accurate to ±0.2 mm. The necessity of making stem corrections was avoided in the dynamic method[3] by suspending the thermometer in the vapor pressure flask. All observed thermometer readings in the static method[4] were corrected for stem exposure. Two series of measurements were made by each method.

It was found that the vapor pressure curve as plotted in the usual manner from the data obtained by the dynamic method[3] of measurement can be expressed by the empirical equation $\log P = -2540.44/T + 8.2059$. Similarly, the corresponding expression for the data obtained by the static

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[1] Messerschmidt, *Ann.*, 208, 97 (1881).

[2] Schuette and Sah, THIS JOURNAL, 48, 3163 (1926).

[3] Ramsay and Young, J. *Chem. Soc.*, 47, 42 (1885).

[4] Smith and Menzies, THIS JOURNAL, 32, 1412 (1910).

method[4] of measurement is $\log P = -2558.42/T + 8.2544$. Furthermore, it was observed that if a composite curve be drawn of the 59 pairs of readings obtained by the two methods of vapor pressure measurement, and an equation fitted to it, there is presented a picture of the relative sensitiveness of these procedures to any decomposition of the lactone that might take place. The deviation plot (Fig. 1) illustrates this situation by showing the differences under the above condition between the observed and calculated pressures at any given temperature. For reasons which will become apparent later, the data obtained by the static method together with the pertinent equation are deemed to be less accurate than the former.

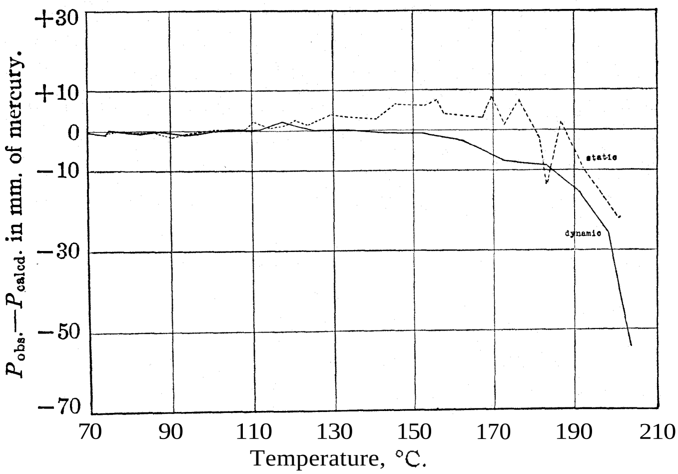

Fig. 1.—Deviation between observed and calculated pressures by two methods of measurement.

Discussion

At the completion of the determination by the Ramsay and Young method, a slight carbonaceous residue was noted in the apparatus where an occasional drop of the lactone had fallen from the thermometer bulb to the hot surface of the flask. The observed pressures for this method agree very well with the calculated up to about 160°, but beyond this temperature there is considerable disagreement, which increases with rising temperature (Fig. 1). Since both of the above facts point to decomposition, it was decided to check these data by using a different method[4] for determining the vapor pressure. Since in this, the isoteniscopic or static, method the material under examination is constantly exposed to view, decomposition becomes visual, if not real, by a change in color of the liquid in question. In this particular instance the lactone showed the first signs of discoloration at about 170°, the color gradually increasing until at the completion of the run it was a dark brown. The observed and calculated values for the vapor pressure again were found to agree very well at low temperatures and to vary considerably at higher temperatures (Fig. 1).

These data bring out the following points: (1) at low temperatures the values for the two methods agree very well; (2) as the temperature increases the pressures recorded by the static method are higher than those by the dynamic; and, (3) in both cases, the observed values are less than the calculated at the higher temperatures.

Conclusion

In the light of the information obtained in this study it appears that n-valerolactone does undergo some decomposition as it approaches its boiling point at atmospheric pressure. This statement is further verified by the darkening of the compound. The isoteniscopic method of determining vapor pressure is in this instance more sensitive to this decomposition. This is due to the fact that the resulting decomposition products are confined to the small space between the liquid in the bulb and in the U-tube rather than being swept out of the apparatus as is the case in the Ramsay and Young apparatus, hence affecting the observed pressure much more. That the values obtained by this latter method actually were lower bears out this conclusion. At first thought it might be expected that if decomposition takes place the observed values would be higher than those calculated. However, this is not necessarily the case since the values log $P/(l/T)$ give a straight line only when the heat of vaporization is a constant with change of temperature. There is no necessity for deeming the heat of vaporization of valerolactone to be a constant; in fact it is very probable that the calculated values would be still lower were it not for the compensating effect of decomposition.

The method most sensitive to decomposition, *i. e.*, the isoteniscopic,[4] does give a better agreement with the calculated pressures at higher temperatures, which justifies the above reasoning.

Summary

1. The vapor pressure of n-valerolactone has been determined and may be expressed by the equation log $P = (-2540.44/T) + 8.2059$, which holds for temperatures up to 160°.

2. It was found that decomposition takes place as n-valerolactone approaches its boiling point at atmospheric pressure.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 51]

A STUDY OF THE BENZOIN CONDENSATION[1]

BY AVERY A. MORTON AND JOSEPH R. STEVENS

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Introduction

In the condensation of benzaldehyde to benzoin under the influence of an alkali cyanide, the specific action of the catalyst has been ascribed, in general, to its ion or to its hydrolysis product. There is a large amount of experimental work which supports this but nearly all has been done in an ionizing solvent which contains water. No systematic attempt has ever been made to observe the reaction under conditions where no ionization nor hydrolysis can occur. In this paper we shall report experiments which show that the reaction will take place in anhydrous petroleum ether, and that an addition compound consisting of one molecule of benzaldehyde and one of sodium cyanide can be obtained, which in the dry state, slowly changes to benzoin. These facts cannot be explained by the common mechanisms. We have, therefore, suggested two possible ways in which the catalyst may function. The results also raise the question as to whether the mechanism in ionizing solvents has been correctly represented in the past.

Experiments

The general experimental method was as follows. Two grams of benzaldehyde (Eastman Kodak Co. technical grade) and one gram of potassium cyanide were put into an 8-inch test-tube with a given amount of the solvent. The test-tube was tightly stoppered and shaken overnight. The contents were then poured into an Erlenmeyer flask, dilute acetic acid added to stop the reaction and the mixture boiled for a short time to volatilize the organic solvent. Any high boiling amines used with the solvent were soluble in the acid solution. The insoluble benzoin was filtered, dried and weighed. A number of these test-tube runs were made at one time. A blank experiment, identical in all respects except that the solvent was 95% alcohol alone, was made with each series. The results are referred to this blank on a basis of 100. Values recorded as (s) slight and (vs) very slight indicate yields of benzoin too small to be measured by our method.

Effect of Solvent

Series 1.—The solvent was 12 cc. of 95% alcohol with 12 cc. of another liquid. The yield in the blank was 1.44 g. of benzoin. Comparative yields were in alcohol with carbon disulfide vs, ethyl bromide vs, ether vs, acetone s, carbon tetrachloride 14, chlorobenzene 31, petroleum ether 120. These results show the marked effect of petroleum ether as compared with carbon disulfide, ether, acetone and certain chlorides.

Series 2.—Twenty-five cc. of a single solvent was used. No effort was made to dry the solvent; in fact, at this stage of the work a trace of moisture was supposed to be favorable in order to hydrolyze the cyanide, Comparative yields were in acetic acid 0,

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[1] From the thesis of Joseph R. Stevens presented in partial fulfilment of the requirements for the degree of Bachelor of Science, 1929.

iso-amyl alcohol vs, tertiary butyl alcohol 6, benzene 47,[2] toluene 52. xylene 55, water 83, methyl alcohol 95.

Series 3.—The comparative yield in a solvent consisting of 20 cc. of 95% alcohol with one gram of phenol was 0, with phthalic anyhdride vs, formaldehyde vs, ethyl acetate vs, isopropyl alcohol 2, aniline 2, hexamethylene tetramine 46, triethylamine hydrochloride 62, benzyl chloride 67, benzal chloride 68, diphenylamine 68, dimethyl aniline 89, hydroquinone 95, pyridine 94, urea 101, acetamide 102, butyl isocyanide 106. The series shows the inhibitory effect of many carbonyl and amine compounds.

The Inhibitory Effect of Ethyl Acetate.--These experiments were made to study the effect of one of the compounds in Series 3 when used in several different concentrations. The solvent was 10 cc. of petroleum ether with 2 cc. of 95% alcohol, this ratio having been found to be very suitable in a number of preliminary tests. Table I gives the results.

TABLE I

RESULTS

KCN, moles	0.02	0.02	0.02	0.03	0.04
Ethyl acetate, moles	.00	.01	.02	.01	.02
Yield of benzoin, g.	.810	.375	.228	.400	.195

Comparison of Sodium Cyanide with Potassium Cyanide. Yield vs. Time.—The solvent was 5 cc. of petroleum ether with 1 cc. of 95% alcohol. An excess of the cyanide (2 g.) was added, which was sufficient to keep the solution saturated at all times with the catalyst and to combine with the product.

The quantities of benzoin formed with potassium cyanide as a catalyst were so very small that only one point could be determined. The results are plotted in Fig. 1. The fact that the values fall on a straight line suggests that the main factor in this solvent is that of the solubility of the catalyst. The solubilities were determined by shaking an excess of the cyanide with the solvent for one hour at room temperature, filtering, evaporating to dryness, and heating in a vacuum oven at 110° to constant weight. The solubility of sodium cyanide was found to be 0.067 mole; that of potassium cyanide 0.0063 mole per liter of solution. The sodium cyanide is therefore 10.6 times more soluble than the potassium cyanide; its reaction velocity is only 6.8 times greater. Since only one point was obtained with potassium cyanide, we are unable to say that this difference is beyond the error of the experiment.

The product from potassium cyanide was white; that from sodium cyanide was yellow. Franzen[3] has prepared the addition compound between calcium cyanide and benzaldehyde and found it to be bright orange-yellow in color. When our sodium cyanide was recrystallized the yellow color largely disappeared. Since sodium cyanide is made from the calcium salt, it is very probable that the orange-yellow color is due to some calcium cyanide present.

Comparison of the Reaction in Alcohol and in Petroleum Ether–Alcohol.—In this series each test-tube contained 6 cc. of 95% alcohol, 2 cc. of benzaldehyde and 2 g. of sodium cyanide. The procedure was identical with that of the experiment just above and the results are plotted in the same figure.

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[2] Conclusions from these series must not be too hastily drawn. The solubility of the cyanide is of very great importance and, as will be shown later, the sodium is much more soluble than the potassium salt. Had sodium cyanide been used in this series instead of potassium cyanide the results for benzene, toluene and xylene might have been very good. The experiments were made to locate any pronounced effect of a solvent and not to assign an absolute value to each.

[3] Franzen, *Ber.*, 42, 3293 (1909).

A constant calculated for this reaction (see Table II) shows that for the first five hours at least the formation of benzoin is in agreement with that expected from the equation for a bimolecular irreversible reaction in which the initial concentration of benzaldehyde is taken as 2 g. The sodium cyanide concentration is assumed to be constant and does not enter into the equation.

TABLE II

RESULTS OF EXPERIMENTS

Time, hours	1.5	2.5	3.5	4.5	5.5
Benzoin, g.	0.52	0.81	0.95	1.05	1.13
K	.12	.14	.13	0.12	0.12

The solubility of sodium cyanide in 95% alcohol was determined in the same manner as in the petroleum ether–alcohol mixture and found to be 0.405 mole per liter. This is six times the solubility of sodium cyanide in the 5:1 mixture. The values as plotted in Fig. 1 show, however, that at no time did the amount of benzoin formed in alcohol even at the very start of the reaction exceed by three times that in the mixed solvent. Per sodium cyanide dissolved, therefore, the reaction is faster in the solvent containing petroleum ether[4] than in alcohol alone. The type of velocity curve is also different with the two solvents. In alcohol the sodium cyanide is so soluble that the formation of benzoin can proceed according to the mass action principle and the customary curves will be obtained; in the petroleum ether–alcohol mixture the sodium cyanide is so slightly soluble and is so continually removed by the precipitation of the addition compound that the rate is governed almost entirely by the rate of solution of the sodium cyanide.

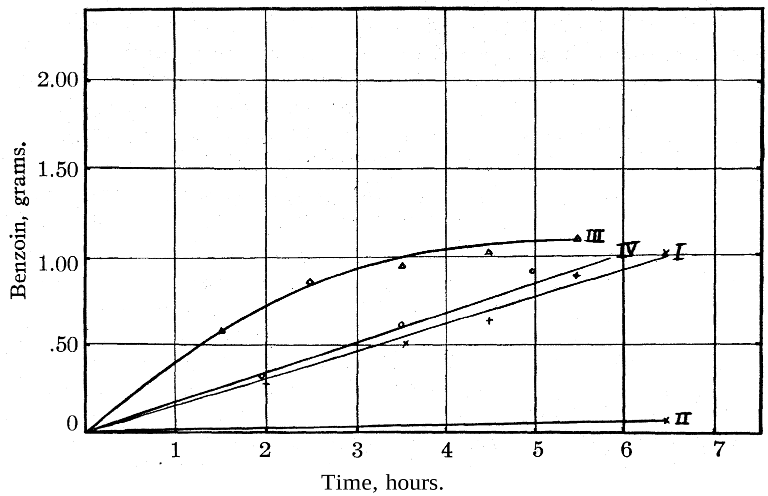

Fig. 1.—I, NaCN in 5:1 mixture of petroleum ether and ethyl alcohol; II, KCN in 5:1 mixture of petroleum ether and ethyl alcohol; III, NaCN in ethyl alcohol; IV, same as I but with purified benzaldehyde.

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[4] The reason for this may be the chemical inertness of petroleum ether. The polar groups present in other solvents would form complexes with the sodium cyanide, thus competing with the benzaldehyde.

Comparison of Technical with Purified Benzaldehyde.—Benzaldehyde was purified by shaking the technical grade with a dilute solution of sodium carbonate, drying over anhydrous potassium carbonate, filtering and distilling. The first 25 cc. out of the 100 cc. was rejected and 2 cc. from the next fraction collected and used at once. This run was made to compare with the results given in Fig. 1, Curve I, for sodium cyanide and the experimental conditions were, therefore, identical in all respects except in regard to the purity of the benzaldehyde. The results are plotted in Fig. 1, Curve IV. The agreement is within 8%, which is as close a check as the experimental conditions would allow.

Isolation of the Addition Compound.—In all of the reactions run in a solvent containing petroleum ether, an addition compound was precipitated. This compound was isolated and analyzed as follows. In a 250-cc. Erlenmeyer flask 3 to 5 g. of sodium cyanide lumps about the size of small peas were placed. A solution of 5 cc. of benzaldehyde in about 30 cc. of the 5:1 petroleum ether–alcohol mixture was added. The mixture was allowed to stand for one-half hour, after which it was shaken and 20 cc. of benzaldehyde added. A large precipitate formed; 100 cc. of petroleum ether was then added and the solution filtered. The large particles of sodium cyanide either settled out before filtration or were mechanically separated from the dried flocculent compound on the paper. The addition product was washed with petroleum ether to free it from benzaldehyde and dried in a vacuum desiccator. Two analyses gave 14.8 and 13.9% of sodium; the calculated value for a product consisting of one molecule of benzaldehyde to one of sodium cyanide is 14.8%. When decomposed with water immediately after removing from the filter paper and drying, benzaldehyde and sodium cyanide were recovered. When allowed to stand in the desiccator over calcium chloride it very slowly changed to benzoin.

Reaction in Anhydrous Medium

Experiment A.—A dry glass tube was sealed off at one end and in it was placed 4–5 g. of sodium cyanide which had been dried in a vacuum oven at 110° for two hours. From 100 cc. of technical benzaldehyde from a freshly opened bottle the first 40 cc. was distilled in a current of dry hydrogen and rejected; 5 cc. of the middle fraction was then distilled directly into the tube aod sealed in an atmosphere of hydrogen. No solvent was used. After two days a precipitate was formed which steadily increased in amount. When decomposed with water this proved to be benzoin.

Experiment B.—A 16-mm. glass tube was heated nearly to its softening point in a current of dry air until no cloud of moisture appeared on the surface of the glass when it was allowed to cool and then reheated. Ten cc. of petroleum ether dried for twenty-four hours over sodium wire, and 3 4 g. of sodium cyanide prepared from commercial sodium cyanide by recrystallizing once from water and drying in a vacuum oven at 110° for four hours, were put into this tube. Ten cc. of benzaldehyde, treated as in Experiment A (except that nitrogen purified by passing through pyrogallol solution and drying with concentrated sulfuric acid was used instead of hydrogen) was distilled directly into the reaction vessel. The tube was then filled with dried nitrogen, sealed off and allowed to stand. A white addition compound formed on the surface of the cyanide; in four days the appearance of benzoin in fair quantity was observed and in ten days a large precipitate had formed.

These experiments do not exclude the possibility of catalysis by an extremely minute quantity of water, but they do show that when the reactants are dried in a manner fully equivalent to that used in reactions where water must be excluded, such as the preparation of the Grignard reagent, the benzoin condensation will still occur. It is necessary only to dissolve the catalyst and to exclude oxygen which would form benzoic acid with the benzaldehyde.

Other Addition Compounds.—Cinnamic aldehyde does not undergo the benzoin condensation. Hence when finely powdered sodium cyanide was added to a solution of an excess of the aldehyde in alcohol, the addition compound was precipitated from the solution and later recrystallized from alcohol. This compound has already been observed but not analyzed by Zincke and v. Hagen.[5] We found 11.1 and 13.0% of sodium as compared with a calculated value of 12.7 for the addition compound, $NaCN{\cdot}C_9H_8O$.

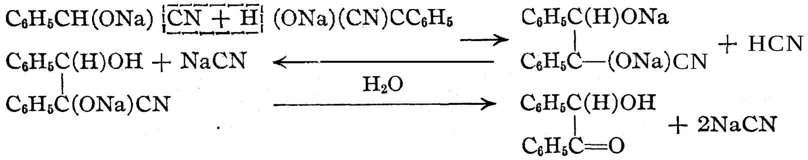
Other addition compounds which were observed but not analyzed were those of sodium cyanide with ethyl benzoate and benzoyl cyanide. Ethyl acetate and benzamide apparently formed no solid addition compound under the conditions of the experiment.

Reaction at Higher Temperature.—Cinnamyl aldehyde[6] will not undergo the benzoin condensation nor will ethyl benzoate condense with benzaldehyde. Since addition compounds are formed in these cases which by their stability might hinder the reaction, higher temperatures were tried. When heated to 150° no condensation occurred in either case. Benzamide and benzaldehyde melted together with sodium cyanide gave off ammonia but nothing was isolated except benzoic acid.

Catalysts Other than Potassium or Sodium Cyanide.—The effect of other compounds as catalysts in this reaction was tried in 10 cc. of the 5:1 petroleum ether–alcohol mixture. About 5 cc. of benzaldehyde and 1 g. of the cyanide compound were used in each experiment. No effect was observed with mercuric, cuprous, thallous, triphenylmethyl, and tertiary butyl cyanides. Barium cyanide had a slight effect. Because sodium cyanide is more soluble[7] than potassium cyanide, it was thought that lithium cyanide would be even more soluble in an organic solvent and therefore a better catalyst. The single attempt to prepare lithium cyanide failed.

Mechanism of the Reaction.—Since the reaction goes in an anhydrous non-ionizing medium it is absolutely impossible to apply the ordinary interpretation to our experiments. It is necessary to consider instead the role of the non-ionized portion. This may be done in two ways. (1) Sodium cyanide may add across the double bond of the carbonyl group. The equations for this would be

$$2C_6H_5CHO + 2NaCN \longrightarrow 2C_6H_5CH(ONa)CN$$



$$C_6H_5CH(ONa)\boxed{CN + H}(ONa)(CN)CC_6H_5 \longrightarrow \begin{matrix}C_6H_5C(H)ONa\\|\\C_6H_5C{-}(ONa)CN\end{matrix} + HCN$$

$$\begin{matrix}C_6H_5C(H)OH\\|\\C_6H_5C(ONa)CN\end{matrix} + NaCN \longleftarrow$$

$$\xrightarrow{H_2O} \begin{matrix}C_6H_5C(H)OH\\|\\C_6H_5C{=}O\end{matrix} + 2NaCN$$

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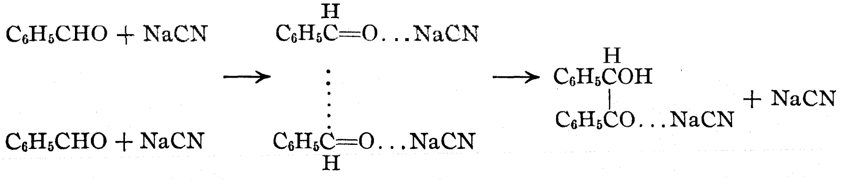
[5] Zincke and v. Hagen, *Ber.*, 17, 1814 (1884).

[6] Cinnamicaldehyde, ethyl acetate, ethyl benzoate and benzamide may not undergo the benzoin condensation because they contain other polar groups in the molecule which combine with the cyanide salt and therefore hinder the reaction in the same manner that ethers, chlorides, alcohols or esters used as solvents block the catalytic influence of the condensing agent. One exception to this is here noted. Smith, *Proc. Chem. Soc.*, *29*, *266* (1913), has reported that benzoyl chloride condenses with *o*-nitrobenzaldehyde in the same manner that benzaldehyde condenses with itself. The product is benzoyl-*o*-nitromandelonitrile, the chlorine atom being replaced by the cyano group.

[7] Tripropylamine cyanide should be a very good catalyst since its organic nature would make it soluble in petroleum ether and Lapworth, *J. Chem. Soc.*, *83*, 1004 (1903), has shown that tripropylamine, mandelonitrile and benzaldehyde form benzoin when allowed to stand together.

This is the nearest approach possible to the common interpretation of the reaction. Its weakness lies in the fact that free hydrogen cyanide instead of a salt must split out to cause the condensation. (2) A molecular addition compound may form which then adds to another molecule of the same kind. The reaction is completed by the wandering of a hydrogen atom in the complex. In the formation of the first intermediate compound the sodium cyanide absorbs some of the valence energy of the oxygen atom in the benzaldehyde. This will cause a certain amount of energy to become available on the carbon atom of the benzaldehyde, *i. e.*, it will possess a certain amount of unsaturation. When two of these addition compounds come close to each other, a valence is realized between the unsaturated carbon atoms with the simultaneous wandering of a hydrogen atom. The steps are graphically represented in the equations



$$\begin{array}{lclcll} C_6H_5CHO + NaCN & & \overset{H}{C_6H_5C}{=}O\ldots NaCN & & & \\ & \longrightarrow & \vdots & \longrightarrow & \begin{array}{l} \overset{H}{C_6H_5COH} \\ \quad | \\ C_6H_5CO\ldots NaCN \end{array} & + NaCN \\ C_6H_5CHO + NaCN & & \underset{H}{C_6H_5C}{=}O\ldots NaCN & & & \end{array}$$

This formulation[S] of the role of an addition compound as an intermediate has been developed by Pfeiffer,[9] who states that the catalytic action of metal salts and acids, which in many cases is dependent upon the formation of addition compounds,[10] can be ascribed to the formation of a single unsaturated active carbon atom. He gives as examples of this the catalytic saponification of esters by hydrochloric acid, the formation of ketones in the Priedel–Crafts reaction, and the polymerization of unsaturated compounds by means of sulfuric acid. This picture gives us a very simple explanation for the occurrence of a side reaction, namely, the formation of benzyl benzoate. If instead of the reaction above pictured the single unsaturated carbon atom in the molecular addition compound should unite with the oxygen of another molecule of benzaldehyde, the product upon the wandering of a hydrogen atom will be benzyl benzoate. The possibilities in the reaction of benzaldehyde with itself in the presence

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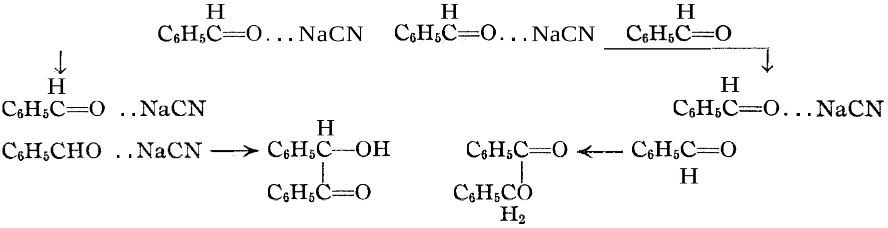
[8] The sodium cyanide might be attached through its unsaturated carbon atom to the benzaldehyde. On this point we have no evidence. We have preferred the formula as above written because metallic sodium alone will cause the condensation and because certain analogies might be drawn with alkaline condensing agents in general and with pinacone formation.

[9] Pfeiffer, *Ann.*, **383,** 93 (1911).

[10] *Sammlung Chemischer und chemisch-technischer Vortrage,* **30,** 136 (1928). Muller expresses Pfeiffer's views by saying that the positive metal ion strongly pulls the electron of the carbon atom. The bonding electrons between the carbon and oxygen atoms then move far toward the oxygen side. The carbon atom which now possesses only a small part of the binding electron will then possess a secondary valence.

of a catalyst such as sodium cyanide are illustrated in the following diagram.



Lachman[11] has shown that benzyl benzoate is formed to some extent in the synthesis of benzoin. In the case of alkali hydroxide or alcoholate addition compounds the formation of benzyl benzoate may be assumed to predominate to the entire exclusion of the formation of benzoin.

This conception[12] also eliminates the peculiar role of the cyanide salts as the only catalysts which can bring about the reaction. Lachman[13] mentions that benzoin is sometimes formed by metallic sodium and Blicke[14] in the same year published a study of the action of sodium on benzaldehyde in which he discovered benzoin among the products.

Summary

A preliminary study of the effect of various solvents upon the benzoin condensation has been made. The reaction has been found to proceed in the absence of water and in a non-ionizing medium.

An addition compound has been isolated which consists of one molecule of benzaldehyde and of sodium cyanide. This solid addition compound changes to benzoin upon standing.

Previous mechanisms which involve ionized or hydrolyzed sodium cyanide are not applicable to our work. Two mechanisms have been suggested which accord with the facts observed. One of these mechanisms is based upon Pfeiffer's view of the role of addition compounds as catalysts.

CAMBRIDGE, MASSACHUSETTS

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[11] Lachman, THIS JOURNAL, **46, 712 (1924).**

[12] **A** similar mechanism might possibly apply to other reactions catalyzed by sodium cyanide. Thus Chalanay and Knoevenagel *[Ber.,* **25,291** (1892)] found that the benzoin condensation took place in the case of certain chlorides and nitriles. Smith *[Ber.,* **26, 60 (1893)]** condensed benzaldehyde with acetophenone, benzoin with acetophenone, and benzoin with mesityl oxide in the presence of potassium cyanide. Strain has shown that benzylidene-aniline and benzylidene-p-toluidine [THIS JOURNAL, 50, **2219** (1928)] undergo the benzoin condensation. In case the mechanism is applicable in ionizing solvents, it might be possible to interpret the action of alkalies in certain condensations such as the Schotten–Baumann reaction on this same basis.

[13] Ref. **10,** p. **716.**

[14] Blicke, THIS JOURNAL, **46, 2560 (1924).**

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

ISOXAZOLINE OXIDES. IX. THE REACTION BETWEEN TRIPHENYL ISOXAZOLINE OXIDE AND ORGANIC MAGNESIUM COMPOUNDS

BY E. P. KOHLER AND N. K. RICHTMYER

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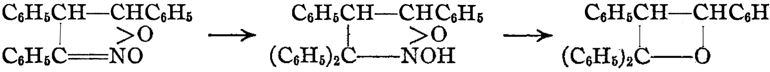
Inasmuch as the mode of addition of organic magnesium compounds to cyclic nitrones has been definitely established,[1] it is possible, now, to interpret with more confidence the results of an investigation of the reaction between organic magnesium compounds and isoxazoline oxides that was completed several years ago. The investigation is one of a series that deals with the mode of addition to substances containing the unsaturated system $>C{=}\overset{|}{N}O$. Triphenyl isoxazoline oxide was one of the compounds selected for study because it contains a highly phenylated ring and therefore might be expected to offer but one point of attack to the reagent. The reaction was tried with methyl, ethyl, benzyl and phenyl magnesium halides, but the outcome was not so favorable as had been anticipated because it was rarely possible to arrest the action at the first stage.

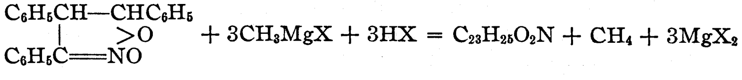
Of all the reagents tried, phenyl magnesium bromide alone gave a product that was formed by the addition of but one molecule of reagent to one of the oxide. The mode of addition appears to be the same as that to the cyclic nitrone, but the product is extremely unstable, decomposing spontaneously both in solution and in solid form. In glacial acetic acid it loses both nitrogen and oxygen and passes into one of the few known derivatives of propylene oxide



$$\begin{array}{l} C_6H_5CH-CHC_6H_5 \\ \quad | \qquad >O \\ C_6H_5C{=}NO \end{array} \longrightarrow \begin{array}{l} C_6H_5CH-CHC_6H_5 \\ \qquad | \qquad >O \\ (C_6H_5)_2C-NOH \end{array} \longrightarrow \begin{array}{l} C_6H_5CH-CHC_6H_5 \\ \qquad | \qquad\quad | \\ (C_6H_5)_2C-O \end{array}$$

I II III

In the reaction with methyl magnesium iodide gas was evolved in the cold. A quantitative determination showed that one molecule of the oxide reacts with three molecules of the reagent and liberates one molecule of methane. The composition of the product confirms this relation, the reaction being represented by the equation



$$\begin{array}{l} C_6H_5CH-CHC_6H_5 \\ \quad | \qquad >O \\ C_6H_5C{=}NO \end{array} + 3CH_3MgX + 3HX = C_{23}H_{25}O_2N + CH_4 + 3MgX_2$$

The product of the reaction is a base. It reacts with methyl magnesium iodide, liberating two molecules of methane and forming a magnesium derivative from which it is regenerated by acids; and when it is acetylated it forms, in succession, a mono- and a diacetyl derivative. It, there-

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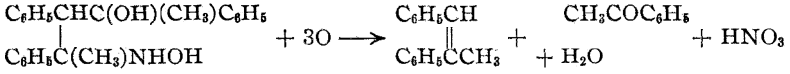
Kohler and Addinall, THIS JOURNAL, 52, 1590 (1930).

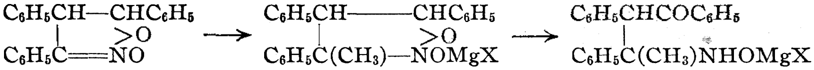
fore, contains two active hydrogen atoms and its two oxygen atoms are presumably present as hydroxyl. In acetone the Grignard product reduces permanganate in the cold, being oxidized to water, nitric acid, acetophenone, and methyl stilbene—all primary oxidation products because permanganate does not oxidize methyl stilbene under these conditions. By combining these facts with the formula of the oxide, we arrive at formula IV for the product, the oxidation proceeding in accordance with the scheme



$$\begin{array}{l} C_6H_5CHC(OH)(CH_3)C_6H_5 \\ \quad | \\ C_6H_5C(CH_3)NHOH \end{array} + 3O \longrightarrow \begin{array}{l} C_6H_5CH \\ \quad \| \\ C_6H_5CCH_3 \end{array} + \begin{array}{l} CH_3COC_6H_5 \\ \\ + H_2O \end{array} + HNO_3$$

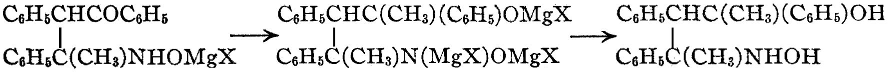
IV

The formation of the hydroxylamine derivative is most easily accounted for by assuming that, in this case also, the reaction begins with addition to the unsaturated system, and that the primary product—an isoxazolidine derivative—immediately undergoes a well-known rearrangement



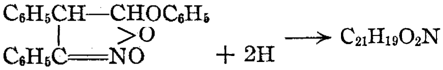
$$\begin{array}{l} C_6H_5CH\text{—}CHC_6H_5 \\ \quad | \qquad >O \\ C_6H_5C\text{=}NO \end{array} \longrightarrow \begin{array}{l} C_6H_5CH\text{———}CHC_6H_5 \\ \quad | \qquad\qquad >O \\ C_6H_5C(CH_3)\text{—}NOMgX \end{array} \longrightarrow \begin{array}{l} C_6H_5CHCOC_6H_5 \\ \quad | \\ C_6H_5C(CH_3)NHOMgX \end{array}$$

The resulting open-chained compound then reacts with two more molecules of the reagent



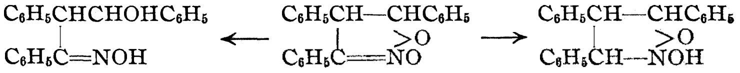
$$\begin{array}{l} C_6H_5CHCOC_6H_5 \\ \quad | \\ C_6H_5C(CH_3)NHOMgX \end{array} \longrightarrow \begin{array}{l} C_6H_5CHC(CH_3)(C_6H_5)OMgX \\ \quad | \\ C_6H_5C(CH_3)N(MgX)OMgX \end{array} \longrightarrow \begin{array}{l} C_6H_5CHC(CH_3)(C_6H_5)OH \\ \quad | \\ C_6H_5C(CH_3)NHOH \end{array}$$

In the case of ethyl magnesium bromide the quantitative picture[2] is far less definite. At the ordinary temperature the reaction consumes 2.8 moles of reagent and liberates 0.6 mole of gas. The gas is not homogeneous, being composed of ethane and ethylene in the proportion of fom to one. The formation of ethane implies a reaction similar to that with methyl magnesium iodide, and the formation of ethylene indicates reduction. No substance corresponding to that obtained with methyl magnesium iodide was isolated. A very small quantity of a substance that appears to be an addition product was obtained, but most of the solid material was a reduction product that is formed in accordance with the equation



$$\begin{array}{l} C_6H_5CH\text{—}CHOC_6H_5 \\ \quad | \qquad >O \\ C_6H_5C\text{=}NO \end{array} + 2H \longrightarrow C_{21}H_{19}O_2N$$

This same reduction product had been obtained previously[3] by reducing the oxide with zinc and acetic acid, and two formulas for it were considered at the time



$$\begin{array}{l} C_6H_5CHCHOHC_6H_5 \\ \quad | \\ C_6H_5C\text{=}NOH \end{array} \longleftarrow \begin{array}{l} C_6H_5CH\text{—}CHC_6H_5 \\ \quad | \qquad >O \\ C_6H_5C\text{=}NO \end{array} \longrightarrow \begin{array}{l} C_6H_5CH\text{—}CHC_6H_5 \\ \quad | \qquad >O \\ C_6H_5CH\text{—}NOH \end{array}$$

V I B

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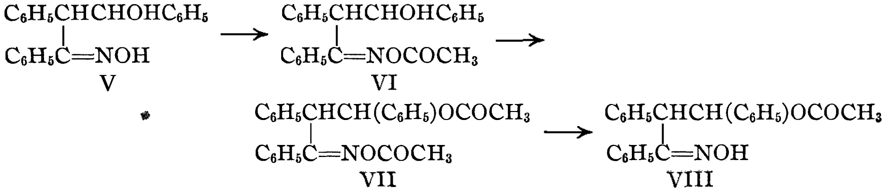
[2] Kohler and Barrett, THIS JOURNAL, 46, 2112 (1924).

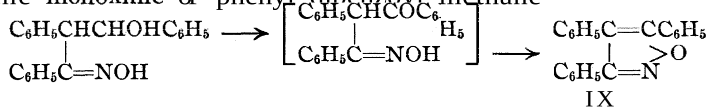
[3] Ref. 2, p. 2110.

The cyclic formula B was preferred to the open-chained formula V largely because the substance is capable of forming a copper derivative. We have now succeeded in getting this copper derivative in a crystalline form, and we have found that it contains one atom of copper to the molecule. It therefore cannot be a derivative of the cyclic form. Moreover, we have found that when the substance is acetylated exhaustively, it forms not only the mono-acetate previously described, but also a di-acetate which on partial hydrolysis passes into a mono-acetate that is isomeric with that obtained by partial acetylation. These facts cannot be reconciled with the cyclic formula. They show that the Grignard product must be the open-chained oxime and that β- as well as α-hydroxy oximes[4] can form copper derivatives when their ethereal solutions are shaken with copper acetate



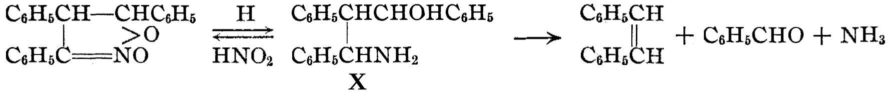
$$\begin{array}{c} C_6H_5CHCHOHC_6H_5 \\ | \\ C_6H_5C{=}NOH \\ \text{V} \end{array} \longrightarrow \begin{array}{c} C_6H_5CHCHOHC_6H_5 \\ | \\ C_6H_5C{=}NOCOCH_3 \\ \text{VI} \end{array} \longrightarrow \begin{array}{c} C_6H_5CHCH(C_6H_5)OCOCH_3 \\ | \\ C_6H_5C{=}NOCOCH_3 \\ \text{VII} \end{array} \longrightarrow \begin{array}{c} C_6H_5CHCH(C_6H_5)OCOCH_3 \\ | \\ C_6H_5C{=}NOH \\ \text{VIII} \end{array}$$

The behavior of the reduction product on oxidation and on further reduction likewise shows that it must be the open-chained oxime. It does not reduce permanganate but it is easily oxidized by chromic acid. The product is triphenyl isoxazole, which, as is known, is readily formed from the monoxime of phenyl dibenzoyl methane[5]



$$\begin{array}{c} C_6H_5CHCHOHC_6H_5 \\ | \\ C_6H_5C{=}NOH \end{array} \longrightarrow \left[\begin{array}{c} C_6H_5CHCOC_6H_5 \\ | \\ C_6H_5C{=}NOH \end{array}\right] \longrightarrow \begin{array}{c} C_6H_5C{=}CC_6H_5 \\ |\quad\;\; >O \\ C_6H_5C{=}N \\ \text{IX} \end{array}$$

On further reduction, which can be accomplished by prolonged heating with zinc and acetic acid, both the Grignard product and the parent isoxazoline oxide are converted into the corresponding amine—a strong base which forms a hydrochloride that is not hydrolyzed by water. Like the oxime, the amine liberates two molecules of methane from methyl magnesium iodide and forms a magnesium derivative from which it is regenerated by acids. When it is heated it decomposes into ammonia, benzaldehyde and stilbene. Its behavior toward nitrous acid is surprising; instead of forming the corresponding di-hydroxyl compound it reverts to the isoxazoline oxide



$$\begin{array}{c} C_6H_5CH{-}CHC_6H_5 \\ |\quad\;\; >O \\ C_6H_5C{=}NO \end{array} \underset{HNO_2}{\overset{H}{\rightleftharpoons}} \begin{array}{c} C_6H_5CHCHOHC_6H_5 \\ | \\ C_6H_5CHNH_2 \\ \text{X} \end{array} \longrightarrow \begin{array}{c} C_6H_5CH \\ \| \\ C_6H_5CH \end{array} + C_6H_5CHO + NH_3$$

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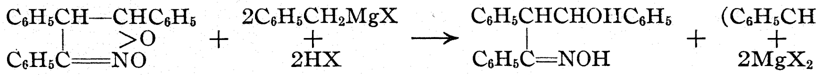
[4] Feigl, Sicher and Singer, *Ber.*, 58, 2294 (1925).

[5] Marshall, *J. Chem. Soc.*, 107, 521 (1915).

The reaction between the oxide and benzyl magnesium chloride is relatively free from complications. Reduction predominates and the principal products are dibenzyl and the same open-chained oxime that is formed, in small quantities, in the reaction with ethyl magnesium bromide



$$\begin{array}{l}C_6H_5CH{-}CHC_6H_5\\ \quad |\qquad >O\\ C_6H_5C{=}NO\end{array} + \begin{array}{c}2C_6H_5CH_2MgX\\ +\\ 2HX\end{array} \longrightarrow \begin{array}{l}C_6H_5CHCHOHC_6H_5\\ \qquad |\\ C_6H_5C{=}NOH\end{array} + \begin{array}{c}(C_6H_5CH_2)_2\\ +\\ 2MgX_2\end{array}$$

Experimental Part

Preparation of Triphenyl Isoxazoline Oxide, I.—Since the oxide prepared according to previous directions[6] often contained triphenyl isoxazole, from which it could not be completely freed by crystallization, it was found necessary to modify the procedure so that no isoxazole would be formed. The operations are as follows: to 9 g. of nitro stilbene and 6 g. of phenyl nitromethane in 100 cc. of gently boiling dry methyl alcohol is added a solution of 0.9 g. of sodium in 50 cc of dry methyl alcohol in the course of three minutes; the solution is allowed to boil for one minute more, then cooled for two minutes by shaking it in a freezing mixture; the mixture of oxide and nitrite is filtered by suction, washed three times with water, then three times with 15-cc. portions of methyl alcohol. The yield is 8.5 g. of oxide melting at 156–159°. Once recrystallized from acetone it melts at 160–162°.

Reaction with Phenylmagnesium Bromide

A Grignard reagent made from 7.5 g. of magnesium and 52 g. of bromobenzene in ether is chilled in ice; to it is added 15.7 g. of solid oxide in the course of two minutes. The mixture is stirred for fifteen minutes, then removed from the ice-bath and stirred for fifteen minutes more. Prolonged stirring is disadvantageous and may result in failure to isolate any solid product.

Decomposition of the reaction mixture is effected by pouring it on ice; crystals appear in the ether layer when the sides are rubbed with a glass rod. A 1:1 mixture of ice and concentrated hydrochloric acid is added to dissolve the basic magnesium salts and then petroleum ether to decrease the solubility of the crystalline product. The mixture is kept cold and stirred for fifteen minutes before filtering. The solid is washed on the filter with water, a little ether, and then thoroughly with petroleum ether.

The Grignard product crystallizes in small colorless needles melting at about 105°, with decomposition. The low melting point implies solvent of crystallization and the analytical results indicate that the crystal solvent is benzene, but since the substance cannot be recrystallized, the significance of the result is doubtful. The substance cannot be benzoylated by the Schotten–Baumann method and an attempt to benzoylate it in pyridine gave but a very small quantity of solid.

2,2,3,4-Tetraphenyl Trimethylene Oxide, III.—When the Grignard product is shaken for an hour with enough glacial acid to cover it, it disappears and the solution gradually deposits the oxide. After washing with ether, the oxide was recrystallized from acetone and methyl alcohol. It separated in diamond-shaped plates melting at 162°.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.5; H, 6.1; mol. wt., 362. Found: C, 89.1; H, 6.0; mol. wt., 340.

Structure and Cleavage.—The structural formula assigned to the oxide is based upon its behavior toward methyl magnesium iodide and upon its cleavage. When it was treated with methyl magnesium iodide in an apparatus with which it is possible to determine both the amount of reagent consumed and the volume of the gas evolved,

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[6] Ref. 2, p. 2109.

it was found that it consumed one mole of reagent and evolved only a negligible volume of gas. The oxide underwent no change when heated to 220° in a vacuum but it was readily cleaved in the following manner.

A solution of one g. of the oxide in 40 cc. of absolute methyl alcohol containing 5 drops of acetyl chloride was heated on a steam-bath for twenty-five minutes. The alcohol was evaporated nearly to dryness, cooled and inoculated; it deposited 0.56 g. of very pure triphenyl ethylene. The filtrate from the unsaturated hydrocarbon was diluted with water and then shaken with ether. From the ethereal solution sodium bisulfite extracted benzaldehyde, which was liberated with sodium carbonate and turned into its phenyl hydrazone for comparison with a known sample.

Dibenzophenone Peroxide, $(C_6H_5)_2CO_2O_2C(C_6H_5)_2$.—Before triphenyl ethylene was available for comparison, a sample of the cleavage product was ozonized in the following manner. A current of ozonized oxygen containing about 5% of ozone was passed through a solution of 4 g. of the hydrocarbon in 30 cc. of dry chloroform. At first, feathery needles appeared on the surface of the vessel; this was, doubtless, the ozonide because it became pasty when rubbed on a drying plate. Later, sharply defined crystals appeared in the liquid. These were separated by evaporating the solvent under diminished pressure, diluting the viscous residue with a little ether and filtering. The crude peroxide was recrystallized from ether.

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.8; H, 5.0; mol. wt., 396. Found: C, 78.6; H, 5.1; mol. wt. (in freezing naphthalene), 350.

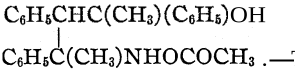
The peroxide dissolves slowly in most organic solvents. It crystallizes from ether in flattened prisms and melts between 200–220°, depending upon the rate at which the temperature is raised. When it is heated with phosphorus pentachloride it liberates chlorine and when it is heated by itself it passes quantitatively into benzophenone and free oxygen.[7]

Reaction between the Oxide and Methyl Magnesium Iodide

The reaction between the oxide and methyl magnesium iodide, when carried out in the "machine"[8] was found to consume 2.92 moles of reagent and liberate 1.11 moles of gas. The evolved gas was collected and analyzed; it was pure methane. For the purpose of isolating the product the oxide was added to a large excess (6 moles) of methyl magnesium iodide at the ordinary temperature. The mixture was left to itself overnight, then decomposed with ice and cautiously treated with acid. At times this treatment left a sparingly soluble iodide, which separated in colorless needles melting at about 100°, and from which the product was liberated with sodium carbonate. Generally the product remained in solution, from which it was isolated by evaporation.

α,γ-Dimethyl-α,β,γ-triphenyl-γ-hydroxy Propylhydroxylamine, IV.—The hydroxyamine was purified by recrystallization from ether–petroleum ether or from dilute alcohol from which it separated in stout needles melting at 180–195°, depending upon the rate of heating.

Anal. Calcd. for $C_{23}H_{25}O_2N$: C, 79.5; H, 7.2. Found: C, 79.1; H, 7.3.

The Monoacetate,  $C_6H_5C(CH_3)NHOCOCH_3$ with $C_6H_5CHC(CH_3)(C_6H_5)OH$ above the C .—The oxime dissolves in cold acetic

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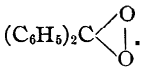
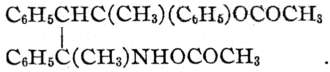
[7] By the action of ozone on a tetraphenyl butene, Lebedev, Andreevski, and Matiushkina [*Ber.*, 56, 2349 (1923)] obtained *a* benzophenone peroxide which began to melt at 170° and which they represent as the monomolecular peroxide  $(C_6H_5)_2C{<}O_2$.

[8] Kohler, Stone and Fuson, THIS JOURNAL, 49, 3181 (1927).

anhydride to form the monoacetate, which was isolated by decomposing the excess of reagent with water and extracting with ether. The substance crystallizes from a mixture of ether and petroleum ether in small prisms; it melts to a colorless liquid which turns yellow and then red between 135–155°.

Anal. Calcd. for $C_{25}H_{27}O_3N$: C, 77.1; H, 6.9. Found: C, 77.7; H, 7.1.



The Diacetate, $\begin{array}{l}C_6H_5CHC(CH_3)(C_6H_5)OCOCH_3\\ \qquad\quad | \\ C_6H_5C(CH_3)NHOCOCH_3\end{array}$.—The diacetate was obtained by warming a solution of the oxime in acetic anhydride for an hour on the steam-bath and then allowing it to evaporate slowly over solid potassium hydroxide in a vacuum desiccator. It was purified by recrystallization from a mixture of ether and petroleum ether; it separated in small needles that melt with decomposition at about 172°. In the machine it liberated only a negligible volume of gas.

Anal. Calcd. for $C_{27}H_{29}O_4N$: C, 75.2; H, 6.7. Found: C, 75.0; H, 6.8.

Oxidation.—The hydroxylamine derivative instantly decolorizes a cold solution of permanganate in acetone. A solution of 3.6 g. of the compound (1 mole) reduced 3.2 g. of permanganate instead of 3.4 g. (2 moles) calculated. The manganese was removed by filtration and the filtrate evaporated to small volume; it deposited potassium nitrate. The acetone solution was then diluted with water and extracted with ether. The ethereal solution on evaporation left an oil. This oily residue was distilled with steam. The first 500 cc. of distillate contained acetophenone, which was recognized by its odor and completely identified by condensing it with meta nitro benzaldehyde.

The remainder of the steam distillate yielded a light-colored oil that solidified when rubbed. This was identified as methyl stilbene by comparison with a sample made by Ley's modification[9] of the method devised by Klages.[10] Methyl stilbene did not reduce permanganate in acetone at the ordinary temperature.

Reaction with Benzyl Magnesium Chloride

To a chilled Grignard reagent made from 7.2 g. of magnesium and 42 g. of benzyl chloride was added 18.9 g. of the oxide. The mixture was left to itself overnight, then decomposed with ice and hydrochloric acid. The ethereal solution yielded 12.3 g. of solid product (V) and the residue that was left after the solid had been removed, on distillation gave 9.7 g. of dibenzyl. The solid crystallized from ether in needles melting between 180–200°, depending on the rate of heating. A comparison of the substance itself and of its monobenzoate with two substances described by Kohler and Barrett[3] proved their identity. In the machine one mole of the substance liberated 2.06 moles of methane and formed a magnesium derivative from which it was regenerated by acids. It therefore cannot have the formula previously ascribed to it.

The Copper Derivative.—An ethereal solution of the hydroxy oxime when shaken with aqueous copper acetate precipitates a very finely divided copper derivative that coagulates as the ether evaporates during persistent filtration under suction. Thus obtained, the copper compound is a dull greenish-brown powder that can be purified by extraction with alcohol and with boiling ether. Upon treatment with 1:1 hydrochloric acid it regenerates the hydroxy oxime.

Anal. Calcd. for $C_{21}H_{17}O_2NCu$: C, 66.6; H, 4.5; Cu, 16.8. Found: C, 65.9; H, 4.8; Cu, 16 5.

The Mono-acetate, VI.—The monoacetate was made by Kohler and Barrett and described as the acetate of the hydroxy isoxazolidine B. It crystallizes with water and melts with decomposition at 100–110°.

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[9] Ley, *Ber.*, 50, 249 (1917).

[10] Klages, *ibid.*, 35, 2648 (1902).

The Di-acetate, **VII.**—The di-acetate was obtained by heating the hydroxy oxime with acetic anhydride on a steam-bath for thirty minutes and then allowing the excess of anhydride to evaporate slowly over solid potassium hydroxide in a vacuum desiccator. The thick oil that remained crystallized readily when moistened with methyl alcohol. The solid crystallized from a mixture of ether and petroleum ether in clusters of large needles melting at 131–132°.

Anal. Calcd. for $C_{25}H_{23}O_4N$: C, 74.8; H, 5.7. Found: C, 74.8; H, 5.8.

The Isomeric Mono-acetate, **VIII.**—A second mono-acetate was obtained by shaking an ethereal solution of the di-acetate for twenty hours with a concentrated solution of ammonia. The ethereal layer deposited small prisms which after recrystallization from a mixture of ether and petroleum ether melted, with decomposition, at 170–176°.

Anal. Calcd. for $C_{23}H_{21}O_3N$: C, 76.9; H, 5.8. Found: C, 76.9; H, 5.9.

Oxidation with Chromic Acid.—A solution of the hydroxy oxime in glacial acetic acid was warmed for five minutes on a steam-bath with an excess of chromic acid. The solution was poured into a large volume of water, and the suspension extracted with ether. The ethereal solution was freed from acetic acid, dried and evaporated. It deposited fine needles of the triphenyl isoxazole (IX)—identified by comparison with a sample on hand.

A small quantity of the oxime of phenyl dibenzoyl methane,[5] which is, doubtless, the intermediate in this reaction, was dissolved in hot glacial acetic acid. The solution began to deposit the isoxazole derivative within thirty seconds.

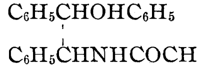
Reduction of Hydroxy **Oxime. α-Hydroxy- γ-amino-α,β,γ-triphenyl** Propane, X—Two g. of zinc dust was added to a solution of the hydroxy oxime in glacial acetic acid diluted with 10% of water. The suspension was warmed on a steam-bath for an hour, then greatly diluted with water and extracted with ether, which removed a small quantity of unchanged oxime. The acid solution, upon neutralization with ammonia, precipitated a white solid which was extracted with ether. The ethereal solution, dried and concentrated, deposited the amine in a yield of 70%.

The same amine was obtained directly from triphenyl isoxazoline oxide by boiling the oxide for six hours with zinc and acetic acid. The yield was 30%

The amine crystallizes from a mixture of ether and petroleum ether in two forms: long glistening needles melting at 123°, and shorter, stouter prisms melting at 128–129°. The melting point of a mixture of the two forms shows no depression, and if the lower melting amine is kept at 120° for ten minutes its melting point becomes 128–129°. Either the needles or the prisms can be obtained at will from an ether–petroleum ether solution by inoculation with the desired form.

Anal. Calcd. for $C_{21}H_{21}ON$: C, 83.2; H, 6.9. Found: (123°) C, 83.2; H, 7.1; (128°) C, 82.6; H, 7.0.

The Hydrochloride.—A benzene solution of the amine was saturated with dry hydrogen chloride and set aside overnight. Since no solid separated from the solution, it was evaporated. The residue was an oil which solidified when ether was added. The solid melted at 232°, dissolved in water without undergoing hydrolysis and regenerated the amine when it was treated with ammonia.

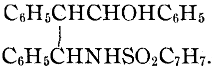


$$\begin{array}{l}C_6H_5CHOHC_6H_5\\ \quad\ |\\ C_6H_5CHNHCOCH_3\end{array}$$

The **Acetyl Derivative,** $C_6H_5CHNHCOCH_3$.—Both forms of the amines are readily acetylated by cold acetic anhydride and they give the same mono-acetyl derivative. This mono-acetyl derivative was also obtained when a solution of the amine in acetic anhydride was warmed for half an hour on a steam-bath, and then allowed to evaporate slowly over potassium hydroxide in a vacuum desiccator. From a mixture of ether and petroleum ether the acetyl derivative crystallized in flattened needles which apparently contain ether of crystallization, because when they are heated rapidly in a capillary tube (plunge method) immediately after crystallization they melt with decomposition at about 135°, while they melt at 142° when heated slowly. After drying overnight at 105°, the melting point is 142° regardless of the rate of heating.

Anal. Calcd. for $C_{23}H_{23}O_2N$: C, 80.0; H, 6.7. Found: C, 79.6; H, 6.8.

In the machine the acetyl derivative consumed 1.9 moles of reagent and liberated 1.9 moles of gas, and it was regenerated when the resulting magnesium compound was treated with acid. It was slowly hydrolyzed to the amine and acetic acid when it was boiled with hydrochloric acid; but it was recovered unchanged after treatment with sodium nitrite in glacial acetic acid. It is, therefore, not the isomeric amino acetate which would be obtained by replacing the hydrogen of the hydroxyl group with an acetyl group.



$$\begin{array}{l} C_6H_5CHCHOHC_6H_5 \\ \qquad\quad | \\ C_6H_5CHNHSO_2C_7H_7 \end{array}$$

The *p*-**Toluene** Sulfonamide, $C_6H_5CHNHSO_2C_7H_7$.—A solution of *0.6* g. of the amine and 4 g. of *p*-toluene sulfone chloride in 10 g. of pyridine was heated for ten minutes, then poured on ice. The resulting suspension was extracted with ether, freed from pyridine, dried and evaporated. It left 0.65 g. of the sulfonamide which, by recrystallization from ether-petroleum ether, was obtained in small prisms melting at 146–148°. It is insoluble in aqueous alkalies and it is precipitated from its solution in methyl alcoholic potash by addition of water.

Anal. Calcd. for $C_{28}H_{27}O_3NS$: C, 73 5; H, 5.9. Found: C, 73.4; H, 6.2.

Action of Nitrous Acid on the **Amine.**—To a solution of 1 g. of the amine in glacial acetic acid was added 0.7 g. of solid sodium nitrite When the formation of gas bubbles had ceased, the solution was poured into water and extracted with ether. The ethereal solution was freed from acetic acid, dried over calcium chloride and evaporated. Addition of petroleum ether to the concentrated solution resulted in the separation of 0.4 g. of triphenyl isoxazoline oxide melting at 155–157°. After one recrystallization from dilute acetone, it melted at 159–161°, and the addition of pure oxide produced no depression in the melting point. A small portion was converted into triphenyl isoxazole to complete the identification.

Thermal Decomposition.—The amine was heated in a small distilling flask until the temperature of the metal-bath reached 330°. Ammonia and benzaldehyde were recognized by their odors and the residue in the flask—which solidified on cooling—was identified as stilbene by comparison with a sample on hand.

Reaction between the Oxide and Ethyl Magnesium Bromide

The reaction with ethyl magnesium bromide has been briefly described by Kohler and Barrett,[2] who obtained a moderate yield of the same reduction product that is formed in the reaction with benzyl magnesium chloride. Since the mechanism by which the oxide is reduced must be very different in the two cases, we have repeated the experiments mainly for the purpose of determining the quantitative relationships. To this end we prepared a solution of ethyl magnesium bromide in iso-amyl ether and with this solution determined the amount of reagent consumed, the volume of the gas evolved and the composition of the gas. We found that 2.8 moles of reagent disappears and that 0.6 mole of gas was liberated. By a suitable contrivance a quantity of the gas was collected over mercury and analyzed. It contained only ethane and ethylene and these were present in the ratio of four to one.

We also repeated the experiment with a reagent made in ethyl ether, but added the oxide to the chilled reagent and decomposed the product an hour later. Under these conditions the amount of reduction produced was much less than that reported by

Kohler and Barrett and in addition to the reduction produced we isolated a small quantity of another solid product. By recrystallization from 50% methyl alcohol this new product was obtained in colorless plates melting at 126°.

Anal. Calcd. for $C_{23}H_{23}O_2N$: C, 80.0; H, 6.7. Found: C, 80.0; H, 6.6.

The composition indicates the addition of C_2H_6 to the oxide, but the substance was obtained in an amount too small for further investigation.

Summary

There are two types of reaction between isoxazoline oxides and organic magnesium compounds.

In one type of reaction the organic magnesium combines at the ends of the unsaturated system $C{=}NO$. The extremely unstable products of this system usually undergo rearrangement to open-chained compounds which react with two more molecules of the reagent.

In another type of reaction the magnesium compounds act as reducing agents. The product of this reaction is an open-chained hydroxy oxime formed by adding two atoms of hydrogen to the oxide.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

STUDIES IN THE DIPHENYL SERIES. II. SOME ANTIMONY DERIVATIVES OF DIPHENYL

BY DAVID E. WORRALL

RECEIVED JANUARY 16, 1930 PUBLISHED MAY 8, 1930

The physiological activity of certain organo-metallic compounds has revived interest and attention to this great class of compounds in the past two or three decades. This has been particularly true of arsenic and in a previous communication[1] some arsenic derivatives of diphenyl were described. While the antimonials have not been as thoroughly studied, it has been found that in certain diseases of protozoan origin they are even more efficacious than arsenicals, a fact that naturally has stimulated work in this field. No work, however, has been done previously in the diphenyl series; therefore some of the more accessible antimonials containing diphenyl have been prepared in this Laboratory and their properties studied.

Tri-biphenylstibine was obtained, using the method of Michaelis and Reese,[2] by the action of an excess of sodium on 4-chlorodiphenyl and antimony chloride dissolved in benzene. The yield was excellent. As in similar condensations with arsenic chloride, diphenyl was formed as a by-prod-

$$3C_6H_5C_6H_4Cl + SbCl_3 + 6Na = (C_6H_5C_6H_4)_3Sb + 6NaCl$$

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[1] Worrall, THIS JOURNAL, **52**, 664 (1930).

[2] Michaelis and Reese, ***Ber.***, **15**, 2877 (1882).

uct. Tri-biphenylstibine instantly decolorized bromine or permanganate solutions because of the ease with which it formed pentavalent antimony derivatives. It did not react with methyl iodide, in this respect differing from tri-biphenylarsine. The halogen addition products, tri-biphenylarsine dichloride, for example, were found to be less sensitive to water than the corresponding arsenic derivatives. In other respects the two series of compounds have similar properties, separating from chloroform solution with a molecule of chloroform, decomposing at the melting point, etc.

The mono- and diarylated derivatives were obtained together by long heating of antimony chloride with tri-biphenylstibine. According to Morgan and Micklethwait[3] two reactions take place with triphenylstibine, the second of which is reversible. The changes would be represented as follows with tri-biphenylstibine

$$2(C_6H_5C_6H_4)_3Sb + SbCl_3 = 3(C_6H_5C_6H_4)_2SbCl$$
$$(C_6H_5C_6H_4)_2SbCl + SbCl_3 \rightleftharpoons 2C_6H_5C_6H_4SbCl_2$$

A fairly good yield of the mixture was obtained, but in the separation by fractional crystallization much material was lost and the amounts of pure substances obtained were much less than the theoretical. Vacuum distillation could not be used, as the substances decomposed. The amount of di-biphenylstibine chloride isolated was about one-fourth of that of mono-diphenylstibine chloride. A certain amount of hydrolysis of tri-biphenylstibine, apparently due to wet material, took place when it was heated with antimony chloride for antimonous oxide and diphenyl were isolated from the products of the reaction and identified.

$$2(C_6H_5C_6H_4)_3Sb + 3H_2O = 6C_6H_5C_6H_5 + Sb_2O_3$$

The low yield of the di-phenylstibine chloride led to a study of the effect of heat on tri-biphenylstibine dichloride in the hope that it might give the desired substance by the reaction

$$(C_6H_5C_6H_4)_3SbCl_2 = (C_6H_5C_6H_4)_2SbCl + C_6H_5C_6H_4Cl$$

Such a decomposition actually took place but additional changes followed, for the quantity of desired product isolated was negligible. Considerable chlorodiphenyl was isolated.

Both mono-diphenylstibine dichloride and di-biphenylstibine chloride when hot gave off irritating vapors, but decomposed when the boiling point was attained. They are readily hydrolyzed and can be changed to stibinic acids by treating with chlorine before hydrolysis.

$$C_6H_5C_6H_4SbCl_2 + Cl_2 + 3H_2O = (C_6H_5C_6H_4)SbO_3H_2 + 4HCl$$

The intermediate tetrachloride may be isolated if desired by working with dry reagents. The stibine acids were air dried at 100° before analysis.

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[3] Morgan and Micklethwait, *J. Chem. Soc.*, **99**,**2286** (1911).

Most of these diphenyl antimony derivatives, as was true of the corresponding arsenicals, decompose when heated; consequently, the melting points vary if the rate of heating changes and are not always easy to reproduce.

Experimental

Tri-biphenylstibine.—To a solution of 100 g. of 4-chlorodiphenyl and 40 g. of freshly distilled antimony chloride in 500 cc. of dry benzene was added an excess (50 g.) of granulated sodium. The mixture was heated under a reflux condenser until boiling started. The reaction subsequently became so vigorous that it was moderated by immersion of the container in ice water. This spontaneous action slackened in about half an hour and heat was again applied for several hours. The product was filtered while hot, the black residue twice extracted with 250 cc. of hot benzene and the combined filtrates concentrated to approximately 250 cc. On addition of an equal volume of warm alcohol the entire mass quickly became semi-solid due to the separation of a bulky crystalline precipitate. It was filtered with difficulty by suction, washed thoroughly with cold alcohol and dried at 100°; yield, 89 g.

Anal. Calcd. for $C_{36}H_{27}Sb$: Sb, 21.0. Found: Sb, 21.2.

The last filtrate was evaporated to dryness and steam distilled. The distillate contaiped diphenyl, identified by its odor and properties, contaminated with some 4-chlorodiphenyl. The residue was not further examined.

Tri-biphenylstibine is easily dissolved by chloroform, methyl iodide or benzene, separating from the latter in microscopic hair-like crystals. It melts at 176.5–177.5" with preliminary softening. Decomposition takes place at the boiling point with the formation of diphenyl and antimony among other things.

Tri-biphenylstibine dichloride, dibromide and di-iodide were obtained by dissolving 5 g. of tri-biphenylstibine in 20 cc. of pure dry chloroform, adding slightly less than the theoretical amount of the corresponding halogen in chloroform and filtering the resulting precipitate. This procedure gave a pure white product, not otherwise obtained With the chloride this precaution was not necessary. The halogen in all cases was instantly absorbed plus considerable heat evolution. The products contained chloroform of crystallization and melted with preliminary softening and decomposition.

	Crystal form	M. p., °C.	Yield. g.	Analysis,[4] %	Calcd.	Found
Dichloride	Small prisms	273–274	5.4	Cl,	9.0	8.9
Dibromide	Narrow plates	259–260	5.6	Br,	18.6	38.4
Di-iodide	Small plates	176–178	6.0	I,	26.6	26.8

Tri-biphenylstibine Hydroxide.—The above halogen derivatives did not react with water, hot or cold, and only slowly with warm 95% ethyl alcohol. Boiling for an hour with alcohol containing ammonia, however, converted them quantitatively into tri-biphenylstibine hydroxide.

Anal. Calcd. for $C_{36}H_{27}Sb(OH)_2$: Sb, 19.8. Found: Sb, 19.6

It is sparingly soluble in hot alcohol, crystallizing out in small flat needles. It begins to sinter at 205° and melts with foaming at 210–211°. The substance is almost insoluble in benzene.

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[4] A weighed amount of the substance after heating for an hour with alcoholic ammonia was evaporated to dryness, extracted with water, and the filtered solution treated in the usual way with silver nitrate. The chloroform of crystallization escaped intact into the air.

Tri-biphenylstibine **sulfide.**[5]—Microscopic needles from the action of hydrogen sulfide on an alcohol solution of the hydroxide.

Anal. Calcd. for $C_{36}H_{27}SbS$: S, 5.2. Found: S, 5.3.

It softens above 168°, melting with foaming at 173°.

Action of Antimony **Trichloride.**—A mixture of 10 g. of tri-biphenylstibine and 8 g. of antimony in 25 cc. of xylene was heated to 220–240° in a sealed tube for 100 hours. The paste-like product was filtered by suction and washed with cold benzene; yield, 9.6 g. The black filtrate on examination was found to contain an appreciable amount of diphenyl.

The solid product proved to he a mixture of two substances difficult to separate and purify. It was dissolved in hot benzene and the resulting cloudy discolored solution filtered while warm. The filtrate on standing deposited crystals which were removed and the new filtrate further concentrated until a new crop of crystals formed. Each lot was dissolved in warm benzene and the process repeated a number of times. Eventually the mixture was separated into two portions, the less soluble consisting of needle-like crystals and the main part of lustrous plates. Slightly more than half a gram of di-biphenylstibine chloride together with two grams of biphenylstibine dichloride was isolated. The final substances probably contained traces of impurities due to hydrolysis, as a slightly cloudy solution formed when benzene was used as a solvent. This cloudiness could be cleared up with hydrogen chloride gas, in harmony with the fact that the chlorides are much more soluble in benzene than the corresponding oxygen derivatives.

Mono-biphenylstibine Dichloride.—Lustrous white plates from benzene melting with preliminary softening at 132–133°.

Anal. Calcd. for $C_{12}H_9SbCl_2$: Cl, 20.5. Found: Cl, 20.4.

The vapors from the hot substance are irritating to the throat, while the skin of the face is slightly sensitive to the solid itself.

Mono-biphenylstibine Oxide.—Obtained as a white powder from the dichloride by the action of alcoholic ammonia. It softens above 155°, melting slowly at 159–160°.

Anal. Calcd. for $C_{12}H_9SbO$: Sb, 41.9. Found: Sb, 42.2.

Mono-biphenylstibinic Acid.—Biphenylstibine tetrachloride was prepared from the dichloride as a thick sirup which partially crystallized on rubbing with a glass rod, by the action of chlorine in chloroform solution and subsequent evaporation of the solvent. It was converted directly by stirring with water into the stibinic acid, a white powder decomposing above 300°.

Anal. Calcd. for $C_{12}H_{11}SbO_3$: Sb, 37.5. Found: Sb, 37.9.

Di-biphenylstibine Chloride.—Obtained by the action of antimony chloride on tri-biphenylstibine.

Anal. Calcd. for $C_{24}H_{18}SbCl$: Cl, 7.6. Found: Cl, 7.8.

It is less soluble than phenylstibine dichloride, separating from benzene in aggregates of small needles. It softens gradually above 150°, melting at 187–188°.

This substance was also obtained by heating tri-biphenylstibine dichloride above its melting point. Foaming occurred and a perceptible odor of chloroform became evident. On further heating the vapors contained chlorodiphenyl and a substance very irritating to the nose. A good yield of 4-chlorodiphenyl was obtained, but the first-formed di-biphenylstibine chloride obviously underwent decomposition, as only traces of it were isolated.

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[5] Sulfur was determined by the method of Carius. The organic matter was not completely destroyed, but the residue after dilution with water was removed and found to be sulfur free.

Di-biphenylstibinic Oxide.—Crystalline powder, melting at 120–121" with preliminary softening, obtained from the preceding chloride by the action of alcoholic ammonia.

Anal. Calcd. for $C_{48}H_{36}Sb_2O$: Sb, 27.9. Found: Sb, 28.1.

Di-biphenylstibinic Trichloride.—Pale yellow flat needles from the action of chlorine on di-biphenylstibine chloride dissolved in chloroform. It softens above 200°, melting at 210°.

Anal. Calcd. for $C_{24}H_{18}SbCl_3$: Cl, 19.9. Found: Cl, 20.0.

Di-biphenylstibinic Acid.—White amorphous powder from the trichloride and alcoholic ammonia. It softens above 201° and melts with decomposition at 204–205°.

Anal. Calcd. for $C_{24}H_{19}SbO_2$: Sb, 26.5. Found: Sb, 26.5.

Summary

Tri-biphenylstibine has been obtained by the interaction in benzene solution of chlorodiphenyl, antimony chloride and sodium.

It is converted into a mixture of mono- and di-biphenylstibine chloride by long heating with antimony chloride. Various tri- and pentavalent antimony derivatives of these substances have been prepared.

TUFTS COLLEGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

RESEARCHES ON CKLORIMINES. I. ORTHO-CHLOROBENZALCHLORIMINE AND ANISALCHLORIMINE

BY C. R. HAUSER AND M. L. HAUSER

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There is evidence[1] that benzalchlorimine has been prepared, but due to its instability it has not been isolated and analyzed. I,uxmoore[2] apparently obtained benzalchlorimine from benz-anti-aldoxime and phosphorus trichloride but the compound decomposed into hydrogen chloride and benzonitrile even below 0°. Later workers[3] apparently obtained impure benzalchlorimine from monochloramine and benzaldehyde but the chlorimine could not be purified as it readily decomposed into hydrogen chloride and benzonitrile.

The decomposition of benzalchlorimine may be represented by the equation, $C_6H_5CH{=}NCl \longrightarrow C_6H_5CN + HCl$. It seemed possible that by substituting electronegative groups in the phenyl radical a more stable chlorimine might result. As a first step in testing this idea, *o*-chlorobenzalchlorimine and anisalchlorimine have been prepared from the corresponding aldehyde and monochlorimine in alkaline solution. Both of these chlorimines are apparently more stable than benzalchlo-

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[1] For evidence see Hauser, THIS JOURNAL, 52, 1108 (1930).

[2] Luxmoore, J. Chem. *Soc.*, 69, 191 (1896).

[3] Forster, *ibid.*, 107, 265 (1915); Raschig, "Schwefel und Stickstoffstudien," 1924, p. 78.

rimine. Furthermore, o-chlorobenzalchlorimine is much more stable than anisalchloriminc. This might be explained by assuming an anti configuration[4] for the former chlorimine and a syn configuration for the latter. However, there seems to be evidence that they are both anti compounds. The analogous oximes have anti configurations[5] when prepared from the corresponding aldehydes and hydroxylamine in alkaline solution, and as the chlorimines were prepared by a similar method, possibly they also have anti configurations. Luxmoore's work[2] indicates that *syn*-benzalchlorimine is so unstable as to be incapable of existence. He found that benz-anti-aldoxime with phosphorus trichloride presumably yielded the anti chlorimine, while benz-syn-aldoxime was instantly converted by the same reagent into benzonitrile, which is the decomposition product of the chlorimine. Of course there is a possibility that the latter reaction was simply a dehydration. It would be interesting to repeat Luxmoore's work with syn and anti aldoximes having electronegative groups in the benzene ring.

o-Chlorobenzchlorimine and anisalchlorimine liberate hydrogen chloride slowly at room temperature and more rapidly as the temperature is raised. If anti configurations for these chlorimines are assumed, then either the elements of hydrogen chloride split off directly from the anti compounds or the anti modifications are first transformed into the syn isomers, which then decompose. A trace of hydrogen chloride might favor such a transformation.[6] The isolation of a second isomer should help to decide this.

Since o-chlorobenzalchlorimine is more stable than anisalchlorimine, chlorine in the ortho position appears to have a greater influence on the stability of the chlorimine than has the methoxy group in the para position. A further study of the stabilizing influences of these and other substituent groups is now in progress.

Experimental

o-Chlorobenzalchlorimine[7] and anisalchlorimine, prepared by the condensation of the corresponding aldehyde with monochloramine[1] in cold aqueous solution, were filtered and washed with cold water. Since crude o-chlorobenzalchlorimine melts around 20°, it is best to use a cooled funnel if the temperature of the room is above 20°. How-

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[4] By analogy with oximes and similar compounds stereoisomeric ald-chlorimines are possible. For stereoisomeric keto-chlorimines, see, Stieglitz and Peterson, *Ber.*, 43, 782 **(1910).**

[5] In this discussion the generally accepted ideas of syn and anti representation are used. Brady and Bishop, however, have presented some evidence that these should be reversed. Brady and Bishop, J. Chem. *Soc.*, **127, 1357 (1925).**

[6] It is interesting to note that although keto-chlorimines could not be induced to change from one isomer to the other by artificial means, the change was effected once when one isomer was allowed to stand for some time. Peterson, *Am. Chem.* **J.,** 46, **325 (1911).**

[7] This chlorimine was previously obtained in an impure condition (see ref. 1).

ever, this precaution is unnecessary in the case of anisalchlorimine as its melting point is higher. A yield of approximately 85% of crude chlorimine was obtained in each case. The chlorimines were recrystallized by dissolving them in 95% alcohol at room temperature, adding just enough water so that the precipitate which formed redissolved on shaking and allowing the solution to stand in an ice-bath or cool place. Since the chlorimines slowly decompose in alcohol as described below, the crystals were filtered shortly after they were formed, pressed on a porous plate until dry and analyzed. Nitrogen was determined by the Kjeldahl method. Active chlorine was determined by treating an alcoholic solution of the chlorimine with potassium iodide solution and concentrated hydrochloric acid and immediately titrating with sodium thiosulfate.

Anal. Calcd. for $ClC_6H_4CH{=}NCl$: N, 8.05; Cl, 20.38. Found: N, 8.07, 8.13; Cl, 20.33, 20.26.

Anal. Calcd. for $CH_3OC_6H_4CH{=}NCl$: N, 8.20; Cl, 20.92. Found: N, 8.19, 8.42; Cl, 20.73, 20.84.

Slightly low results for nitrogen were obtained when anisalchlorimine, either free or in alcoholic solution, was allowed to stand for some time in concentrated hydrochloric acid and then neutralized and distilled into standard acid. Results are liable to be low for active chlorine unless the determination is carried out rapidly using well cooled solutions.

o-Chlorobenzalchlorimine, $ClC_6H_4CH{=}NCl$.—This substance was obtained as small white crystals and melted at 27–29°. By recrystallizing very slowly, small needles were obtained which melted at 28–29°. When the chlorimine was heated above its melting point, a temperature was reached at which it suddenly decomposed rather violently. This decomposition temperature ranged from 120–160°, depending upon the rate of elevation of temperature and possibly upon other factors. About 0.5 g. of one preparation in a small test-tube was immersed in a bath at 146° and the temperature gradually raised to 155°, when the chlorimine suddenly decomposed rather violently, evolving fumes of hydrogen chloride and leaving a residue from which o-chlorobenzonitrile was isolated. The nitrile was identified by the mixed melting point method and by hydrolysis to the corresponding acid.

o-Chlorobenzalchlorimine kept in a desiccator over solid sodium hydroxide for several hours at room temperature was shown by analysis for active chlorine to be practically unchanged. Even after five days an analysis showed that about 90% of the chlorimine remained unchanged.

The chlorimine is also quite stable in benzene solution. A benzene solution of the chlorimine was allowed to stand at room temperatures (18–24°) for fifteen days. When the benzene was allowed to evaporate, an oil was obtained which was identified as slightly impure o-chlorobenzalchlorimine. Recrystallization from alcohol yielded the pure chlorimine.

The chlorimine slowly decomposed in alcoholic solution yielding principally o-chlorobenzaldehyde. The phenylhydrazone of this aldehyde was prepared and identified by the mixed melting point method. Since alcohol was used as the crystallizing solvent, the following preliminary experiment was performed in order to determine whether the rate of decomposition of the chlorimine in alcoholic solution was appreciable. The decomposition of the chlorimine in 95% alcohol solution (approx. 0.2 M) at 12–18° was followed by titrating a 10-cc. portion of the solution with sodium thiosulfate immediately after the solution was prepared and then every twenty-four hours until the decomposition was complete. At the end of the first twenty-four hours the amount of thiosulfate required was practically the same as the amount required for the initial titration. At the end of forty-eight hours a slightly smaller amount of thiosulfate was required. The decomposition then proceeded more rapidly until it was practically complete after five or six days. The acidity of the solution increased as the decomposition proceeded. The increased acidity, due perhaps to the decomposition of some chlorimine or possibly some ethyl hypochlorite, apparently accelerated the rate of hydrolysis of the chlorine. A more detailed study of this will be made.

Anisalchlorimine, $CH_3OC_6H_4CH{=}NCl$.—This substance, obtained as well-formed white crystals from alcohol, melted at 43–44" when it was immersed in a bath at 40° and then heated gradually. Due perhaps to slight decomposition the chlorimine began to soften at a lower temperature when the melting point was determined in the usual way. Similarly to o-chlorobenzalchlorimine, when antsalchlorimine was heated above its melting point, a temperature was reached at which the substance decomposed rather violently into hydrogen chloride and the nitrile. This decomposition temperature varied from **60** to 85°. Doubtless some decomposition occurred at lower temperatures but due to the greatly increased rate of decomposition at higher temperatures the chlorimine appeared to decompose all at once. Sometimes this reaction was almost explosive in nature. When the chlorimine in a melting point tube was immersed in a bath at 69–70° over two minutes elapsed before sudden decomposition occurred. However, at 81–82" violent decomposition took place after several seconds. When a small amount of one preparation was kept at 65° for several minutes the inside of the tube became coated with a white solid. However, when a larger quantity, about 0.5 g., was immersed in a bath at 65" for several seconds, it decomposed violently, evolving hydrogen chloride and leaving a residue from which the nitrile and imine hydrochloride were isolated. Evidently the heat of decomposition of some of the chlorimine raised the temperature of the rest so that the decomposition became violent. The nitrile was identified by the mixed melting point method and by hydrolysis to the corresponding acid. The imine hydrochloride was hydrolyzed to anisaldehyde, which was identified by the preparation of the phenylhydrazone.

Anisalchlorimine decomposes at room temperature more rapidly than o-chlorobenzalchlorimine. After standing in a desiccator over solid sodium hydroxide for twenty-four hours, an analysis for active chlorine indicated that only 8% of the chlorimine remained unchanged. After five days the material had a mouldy appearance and an analysis showed that only a trace of active chlorine was left. When 0 873 g. of this material was warmed with several small portions of anhydrous ether and filtered, **0.346** g. remained as the insoluble portion; calculated by difference, 0.527 g. of the material was dissolved by the ether. When the ether was evaporated about 0.4 g. of residue was obtained, which after recrystallizing from ligroin was identified as anisic nitrile by the mixed melting point method and by hydrolysis to the corresponding acid. The fraction of material insoluble in ether was shown to consist almost entirely of the imine hydrochloride The latter compound was hydrolyzed to ammonium chloride and anisaldehyde and the phenylhydrazone of the aldehyde was prepared. The decomposition of the chlorimine may therefore be represented by the equations

$$2CH_3OC_6H_4CH{=}NCl \longrightarrow 2CH_3OC_6H_4CN + 2HCl$$
$$CH_3OC_6H_4CH{=}NCl + 2HCl \longrightarrow CH_3OC_6H_4CH{=}NH\cdot HCl + Cl_2$$

A crude portion of the chlorimine after standing for several hours in a desiccator spontaneously decomposed rather violently, evolving fumes of hydrogen chloride and leaving a brown residue from which the nitrile was isolated.

Apparently anisalchlorimine also decomposed in benzene solution according to the above equations. After a benzene solution had stood at room temperatures (18–24°) for several days, chlorine was detected above the solution by means of starch–potassium iodide paper. After fifteen days the benzene was allowed to evaporate, and the residue obtained was shown to consist principally of the imine hydrochloride and the nitrile.

Since anisalchlorimine in alcoholic solution yielded principally anisaldehyde, apparently an hydrolysis similar to that described for o-chlorobenzalchlorimine occurred.

Reduction of Anisalchlorimine to *o*-Methoxybenzylamine.—Two grams of the chlorimine in alcoholic solution was reduced with sodium amalgam at about 30° by the method described in a recent paper.[1] A 64% yield of white crystals of amine hydrochloride was obtained.

Anal. Calcd. for $C_8H_{11}ON \cdot HCl$: N, 8.05. Found: N, 8.04.

Summary

o-Chlorobenzalchlorimine and anisalchlorimine were prepared from the corresponding aldehyde and monochloramine. Since the former chlorimine is more stable than the latter, chlorine in the ortho position apparently has a greater influence on the stability of the chlorimine than has the methoxy group in the para position.

The chlorimines decompose slowly at room temperatures and more rapidly as the temperature is raised into hydrogen chloride and the corresponding nitrile.

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[Contribution from the Chemical Laboratory of the University of Illinois]

STEREOCHEMISTRY OF DIPHENYL COMPOUNDS. V. PREPARATION AND RESOLUTION OF 2,4,6,2',4',6'-HEXANITRO-3,3'-DICARBOXYDIPHENYL[1]

By L. H. Bock, W. W. Moyer[2] and Roger Adams

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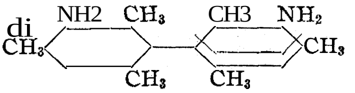
The resolution of 2,4,6,2',4',6'-hexamethyl-3,3'-diaminodiphenyl (I)[1b] (diaminodimesityl) demonstrated that the groups in the 2,6,2',6'-positions in diphenyl could all be methyl and still render the molecule capable of existing in optically active forms. The conclusion from this research was that probably any group in place of the methyl would be equally satisfactory for producing similar results providing it is sufficiently large.

In this investigation the preparation of a compound containing four nitro groups in the 2,2',6,6'-positions was undertaken and the specific compound studied was 2,4,6,2',4',6'-hexanitro-3,3'-dicarboxydiphenyl (II).



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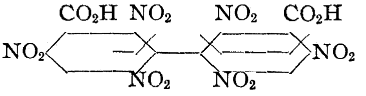

II

This substance is of particular interest as compared to diaminodimesityl because of the entirely different electrochemical character of the nitro

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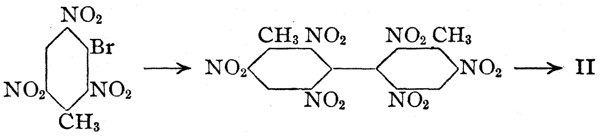
[1] Previous papers in this field are: *(a)* Hyde and Adams, This Journal, 50, 2499 (1928); (b) Moyer and Adams, *ibid.*, 51, 630 (1929); (c) Stanley and Adams, Rec. *trav. chim.*, 48, 1035 (1929); (d) This Journal, 52, 1200 (1930).

[2] This communication is an abstract of portions of theses submitted by W. W. Moyer and L. H. Bock in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

and methyl groups, due chiefly to the extra unshared electrons in the former. It was found that this compound could be readily resolved through the strychnine salt.

The optically active isomers were resistant to racemization. Ten hours of refluxing in glacial acetic acid or twelve hours of heating at 90–95° in 5% ammonium carbonate solution resulted in essentially no change in rotation. A cold 5% solution of sodium bicarbonate had no effect and heating in the same solution for one and one-half hours at 100° changed the rotation only about 4%. Since this latter treatment caused a coloring of the solution, it is likely that decomposition may have accounted for the slight change. The x-ray data presented in the previous paper would lead to the expectation that the optically active 2,2′,6,6′-tetranitro-3,3′-dicarboxydiphenyl would have no tendency to racemize.

The 2,4,6,2′,4′,6′-hexanitro-3,3′-dicarboxydiphenyl was prepared by nitration of 3-bromotoluene to the trisubstituted derivative (III), condensation of this to 2,4,6,2′,4′,6′-hexanitro-3,3′-dimethyldiphenyl (IV) and oxidation of the methyl groups to the dibasic acid (II).



III IV

The condensation of trinitrobromotoluene to the diphenyl derivative by means of copper was accomplished only after very carefully regulated conditions were discovered. Successful results were obtained with nitrobenzene as a solvent and a temperature about 10° below the point where trinitrobromotoluene and copper give a vigorous exothermic reaction. The oxidation of the condensation product took place readily with a mixture of sodium dichromate, sulfuric acid and fuming nitric acid. The final acid showed no signs of resolution with brucine or quinine but readily separated into two salts with strychnine. Hexanitrodicarboxydiphenyl did not lose carbon dioxide readily, as after heating in various solvents there were no signs of decomposition.

A few words concerning the unsuccessful experiments to obtain 2,4,6,2′,4′,6′-hexanitro-3,3′-dimethyldiphenyl and other compounds with the 2,6,2′,6′-position filled with nitro groups should be included. (1) 3,3′-Dimethyldiphenyl, which was readily prepared by the action of 3-tolylmagnesium bromide with cupric chloride could, in spite of many experiments, be nitrated only to the tetranitro compound with only two of the nitro groups undoubtedly in the desired positions. (2) From tolidine by tetrazotization and treatment with cuprous cyanide, 3,3′-dimethyl-4,4′-dicyanodiphenyl was obtained which was then hydrolyzed to 3,3′-dimethyl-4,4′-dicarboxydiphenyl. Nitration gave what at first appeared to be the desired 2,6,2′,6′-tetranitro compound. A few attempts at resolution failed but no exhaustive study was made owing to the uncertainty of the constitution of the product. (3) Through the 4-chloro derivative of *o*-acetoluidide by hydrolysis, diazotization, introduction of the cyano group and hydrolysis, 4-chloro-2-methylbenzoic acid was obtained. Contrary to the reports in the literature, no dinitro compound could be obtained which it was hoped might be esterified and condensed with copper to the diphenyl derivative, 2,6,2′,6′-tetranitro-4,4′-dicarboxy-3,3′-dimethyldiphenyl.

Experimental

2,4,6-Trinitro-3-bromotoluene.—The preparation was carried out in two steps Dinitro-3-bromotoluene was prepared first as suggested by Grete[3] by the nitration of 3-bromotoluene and then further nitrated to the trinitro compound by the method of Bentley and Warren.[4]

2,4,6,2′,4′,6′-Hexanitro-3,3′-dimethyldiphenyl.—In a 500-cc. three-necked flask fitted with a thermometer and a mechanical stirrer was placed a solution of 110 g. of trinitrobromotoluene in 320 cc. of nitrobenzene. The flask was heated on an oil-bath to 160°, at which point about 5 g. of copper powder (Kahlbaum's Naturkupfer C) was added and the temperature slowly raised to 175° with constant stirring. At this temperature the reaction begins to take place as evidenced by the loss of metallic luster of the copper and a rise in temperature. The flame under the oil-bath was turned low and the temperature was maintained at 175–183° by adding copper powder slowly until 110 g. in all had been used. A higher temperature than 183° must be avoided since this results in a tarry product difficuit to purify. The mixture was stirred for one-half hour at 175–180° after all the copper powder was added. The flask was then allowed to cool and the copper residue was filtered off and washed with acetone. The filtrate and washings were combined and subjected to steam distillation to remove all the nitrobenzene. The product was filtered from the water in the flask, dissolved in about one liter of acetone and refluxed for an hour with 25 g. of norite. The norite was filtered off and the acetone was removed by distillation until the volume was about 100 cc. When allowed to stand for several hours the hexanitromethyldiphenyl crystallized in yellow granular crystals. The product was recrystallized from glacial acetic acid. Fifty-seven grams (70%) of a light yellow product melting at 240–241° was obtained. Hexanitrodimethyl diphenyl is practically insoluble in alcohol and ether but very soluble in acetone. It dissolves in warm benzene, toluene and acetic acid.

Anal. Calcd. for $C_{14}H_8O_{12}N_6$: H, 1.78; C, 37.16. Found: H, 1.87, 1.90; C, 36.72, 37.1.

2,4,6,2′,4′,6′-Hexanitro-3,3′-dicarboxydiphenyl.—A solution was made of 33 g. of hexanitrodimethyldiphenyl in a mixture of 330 cc. of fuming nitric acid (1.52 sp. gr.; moreover, the acid must be of superior grade to give good results) and 115 cc. of 20% fuming sulfuric acid. The solution was placed in a one-liter three-necked flask equipped with a thermometer and a mechanical stirrer. The mixture was cooled to 20° with stirring and 120 g. of sodium dichromate was added slowly over a period of one-half hour. The temperature was maintained below 30°. The temperature rises very slowly and the reaction requires attention for two hours or more in order to maintain the

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[3] Grete, Ann., 177, 258 (1875).

[4] Bentley and Warren, Am. *Chem.* J., 12, 4 (1800).

proper temperature. The mixture was stirred for twenty hours at room temperature and poured into one kilo of cracked ice. A white powdery precipitate was formed which was filtered off and washed with 20% hydrochloric acid. The solid was dissolved in 250 cc. of cold alcohol and filtered to remove any insoluble unreacted material. The filtrate was treated with concentrated hydrochloric acid to reprecipitate the hexanitrodicarboxydiphenyl. This was filtered and recrystallized from one liter of benzene. A yield of 27 g. (72%) of pure acid was obtained, melting at 292–293°. Hexanitrodicarboxydiphenyl is colorless when pure but rapidly turns yellow when allowed to stand in the air. For this reason it was always dried in a vacuum desiccator. It is very soluble in acetone, alcohol and ether, and warm water. It dissolves slowly in boiling benzene and separates as long colorless needles on cooling.

Anal. Calcd. for $C_{14}H_4O_{16}N_6$: N, 16 41. Found: N, 16 14, 16.57.

Resolution of **2,4,6,2′,4′,6′-Hexanitro-3,3′-dicarboxydiphenyl.**—A solution of 10 g. of hexanitrodicarboxydiphenyl was dissolved in 500 cc. of methyl alcohol and added to 13.5 g. of strychnine dissolved in 3 liters of methyl alcohol. The solution was allowed to stand for several hours and the salt was filtered off. Concentration of the mother liquor showed that practically all of the salt had separated. The salt was dissolved in a mixture of one-third pyridine and two-thirds water by volume and crystallized slowly. The first fractions were recrystallized three times from the same solvent to obtain the maximum levo rotation. The soluble fraction separated as a gum on concentrating the mother liquors. By adding acetone to these mother liquors, the gum crystallized. Two recrystallizations yielded a salt of constant dextro rotation. The yields obtained were about 6 g. of 1-salt and 4 g. of d-salt.

I-Salt. 0.1080 made up to 15 cc. with pyridine at 20° gave a, − 0.54; $l = 1$, $[\alpha]^{20}_{\text{D}}$ −74.7°.

d-Salt. 0.1171 made up to 15 cc. with pyridine at 20° gave a, 0.47, $l = 1$, $[\alpha]^{20}_{\text{D}}$ +60.0°.

No sharp melting point could be obtained for either salt as they decomposed above 250°, the 1-salt decomposing at a slightly higher temperature.

Anal. Calcd. for $C_{56}H_{48}O_{20}N_{10}$: H, 4.1, C, 56.93. Found: *l*-salt—H, 4.0; C, 57.4. *d*-salt—H, 4.2; C, 58.04.

It was found impossible to resolve this compound either by means of brucine or quinine. Attempts to resolve by adding portions of strychnine to the acid and fractionally precipitating salt in this way gave variable results due, probably, to the separation of both normal and acid salt in the fractions.

d- and **l-2,4,6,2′,4′,6′-Hexanitro-3,3′-dicarboxydiphenyls.**—The active acids were liberated from the active salts by treating with hydrochloric acid in alcohol. To a mixture of 150 cc. of 95% alcohol and 40 cc. of concentrated hydrochloric acid was added 4.5 g. of 1-salt. The mixture was placed in a 500-cc. round-bottomed flask and stirred at 60° for two hours. The mixture was then cooled and 50 cc. of concentrated hydrochloric acid was added to insure the complete precipitation of the free acid. The mixture was then cooled to 0° and filtered. The solid obtained was redissolved in 95% alcohol, filtered to remove any undecomposed salt and again precipitated with hydrochloric acid. A yield of 2 g. of acid was obtained. The acid was recrystallized by dissolving in acetone and concentrating until crystals started to separate. An equal volume of benzene was then added and the solution allowed to stand until the acid had all crystallized. A pure acid was then readily obtained but the recovery was very poor. The product melts with decomposition at about 230–240°.

1-acid: 0.1143 g. made up to 15 cc. with acetone at 20° gave α_{D} −0.17°, 1 = 1, $[\alpha]^{20}_{\text{D}}$ −21.84'. 0.2230 g. made up to 25 cc. with acetic acid at 20° gave a, −0.24°, $l = 1$, $[\alpha]^{20}_{\text{D}}$ −27.22'. 0.1034 g. made up to 15 cc. with 5% $NaHCO_3$ solution at 20°

gave α_D −0.55°, 1 = 1, $[\alpha]_D^{20}$ −80.5". 0.1377 g. made up to 25 cc. with 5% $(NH_4)_2CO_3$ solution at 20° gave α_D −0.37°, l = i, $[\alpha]_D^{20}$ −66.74".

The d-acid was obtained from the d-salt by similar treatment. To a mixture of 15 cc. of 95% alcohol and 5 cc. of concentrated hydrochloric acid was added 0.6 g. of d-salt, On stirring, the salt completely dissolved, showing that it decomposed readily in the cold. An additional 5 cc. of concentrated hydrochloric acid was added to precipitate the free acid, and it was purified by the same method as used with the I-acid. About 0.2 g. of d-acid was obtained.

d-Acid. 0.0555 g. made up to 15 cc. with 5% $NaHCO_3$ solution at 20° gave a, +0.29°, 1 = 1, $[\alpha]_D^{20}$ +79.67°.

Racemization Experiments on Active Acids

1. A solution of 0.223 g. of 1-acid in 25 cc. of glacial acetic acid was prepared and the initial specific rotation was [or]? −27.22°. The solution was heated for four hours at 100" in a flask connected with a reflux condenser by a ground-glass connection. The solution showed no change in rotation. The solution was then refluxed for ten hours, when it showed a slightly increased rotation which was probably caused by the concentration of the acetic acid through loss from the top of the condenser. The acid was precipitated by adding an equal volume of concentrated hydrochloric acid. The acid so precipitated was filtered and dried in a vacuum desiccator and the rotation determined.

0.0528 g. made up to 15 cc. with 5% $NaHCO_3$ solution at 20° gave α_D − 0.26°, 1 = 1, $[\alpha]_D^{20}$ −73.89".

2. A 5% sodium bicarbonate solution was made and rotations were read at intervals for three days during which time the solution was stored in a dark place at room temperature.

Initial Rotation.—0.1034 g. made up to 15 cc. with 5% $NaHCO_3$ solution at 20° gave α_D −0.55°, l = 1, $[\alpha]_D^{20}$ −80.5°. Rotation after eighty *hours*.—α_D −0.53°, l = 1. $[\alpha]_D^{20}$ −76.5°.

3. A sodium bicarbonate solution was heated on a steam-bath for one and one-half hours. At the end of this time it was becoming colored so the heating was not continued. The solution was not made up to standard volume but the rotation changed from an initial reading of α_D −0.28" to a final reading of α_D −0.26". The changing of color may have affected the rotation here as in the experiment described above. Sodium carbonate solution could not be used as it became deep red on short standing.

4. A sample of 1-acid was heated in a 5% ammonium carbonate solution for twelve hours on a water-bath at 85–95° The solution did not become colored.

Initial rotation.—0.1377 g. made up to 25 cc. with 5% $(NH_4)_2CO_3$ solution at 25° gave α_D −0.37°, l = 1, $[\alpha]_D^{20}$ −66.74°. Rotation after twelve hours of heating.—a, −0.35"; l = 1, $[\alpha]_D^{20}$ −62.96°.

3,3'-Dimethyldiphenyl.—A Grignard solution was prepared from 342 g. of pure 3-bromotoluene and 49 g. of magnesium turnings in 750 cc. of dry ether and a few crystals of iodine. A suspension of 300 g. of finely powdered anhydrous cupric chloride in 600 g. of ether was added with stirring while the flask was cooled with ice. The mixture was refluxed overnight. Decomposition by pouring on ice and hydrochloric acid yielded 3,3'-dimethyldiphenyl, which distilled at 138–139° at 5 mm. The yield was 118 g. (64%).

Tetranitro-3,3'-dimethyldiphenyl.—To 50 g. of fuming nitric acid cooled to −5° was added slowly, with vigorous stirring, 10 g. of 3,3'-dimethyldiphenyl. The temperature was not allowed to rise above 0° during the whole addition. Then, with stirring, 50 g. of concentrated sulfuric acid was added and the temperature allowed to go up to 60–70°. The mixture was stirred for two hours and then poured on cracked ice. The white product was filtered, washed, dried and recrystallized from 250 cc, of glacial acetic acid until pure. Nine g. of light-yellow crystals of a constant melting point at 234" (corr.) was obtained.

Anal. Calcd. for $C_{14}H_{10}O_8N_4$: C, 46.40; H, 2.78. Found: C, 46.78; H, 2.87.

The acetic acid filtrate from the first recrystallization, upon dilution with water, gave a gummy material, which was recrystallized many times from alcohol. Finally, a substance melting over the range 102–110° was obtained which was not identified.

All attempts at further nitration by heating with fuming nitric and fuming sulfuric acids under varying conditions were unsuccessful.

3,3′-Dimethyl-4,4′-dicarboxydiphenyl.—A solution of 210 g. of concentrated sulfuric acid and 140 g. of water was heated to 160° in a 2-liter, three-necked flask fitted with stirrer, thermometer and reflux condenser. 3,3′-Dimethyl-4,4′-dicyanodiphenyl[5] was added, with vigorous stirring, in small amounts to the hot acid solution. A deep purple color at first appeared, but faded with the separation of a grayish solid. Hydrolysis was continued for five hours at 150–160°, with constant stirring. The reaction mixture was poured into ice water and filtered. The acidic product was dissolved in dilute alkali solution and decolorized with norite. By the addition of hydrochloric acid, the product came down as a gelatinous mass that could not be filtered dry by suction. The wet acid was dried in a vacuum oven at 120°. The weight of crude acid was 71 g., the extra weight over the calcd. 64 g. being due to the inorganic salt occluded in the gelatinous mass. The compound was not further purified, but pulverized, and used in the nitration as such.

Nitration of 3,3′-Dimethyl-4,4′-dicarboxydiphenyl.—In a 1-liter, three-necked flask fitted with a thermometer and mechanical stirrer, was placed 300 g. of fuming nitric acid. The flask was surrounded by an ice-salt freezing mixture and the nitric acid cooled to −5°. Then, with stirring, the 71 g. of crude 3,3′-dimethyl-4,4′-dicarboxydiphenyl described in the last preparation was added in small amounts, while the temperature was kept at 0° or below. Then, through a separatory funnel was added 700 g. of 15% fuming sulfuric acid. The temperature rose to 65°, at which point a solid began to separate from the solution, with foaming. The mixture was stirred for an hour at 65° and then heated to 90° for one-half hour. The cool nitration mixture was poured on cracked ice and the product filtered. The crude product was dissolved in dilute ammonium hydroxide solution and reprecipitated with hydrochloric acid. After filtering and washing the weight was 78 g.

The nitro compound was then decolorized by boiling with norite in 600 cc. of alcohol. The alcohol filtrate from the norite was heated to boiling and hot water was added until turbidity was noticed. On cooling, 40 g. of yellowish-white crystals, powder-like in fineness, were obtained. The melting point was 320–350° with decomposition.

Anal. Neut. equiv. Subs., 0.2070 g. required 12.0 cc. of 0.0733 *N* alkali. Calcd. mol. wt.: 225. Found: 235.

After four crystallizations from dilute alcohol, a product with a neutral equivalent of 227 was obtained. The melting point range was 330–350° due to decomposition dependent upon the rate of heating.

Anal. Calcd. for $C_{16}H_{10}O_{12}N_4$: C, 42.66; H, 2.24. Found: C, 42.66; H, 2.29

Summary

1. 2,4,6,2′,4′,6′-Hexanitro-3,3′-dicarboxydiphenyl has been prepared by condensing 2,4,6-trinitro-3-bromotoluene with copper and oxidizing the resulting 2,4,6,2′,4′,6′-hexanitro-3,3′-dimethyldiphenyl with a mixture of fuming nitric acid, sulfuric acid and sodium dichromate.

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[5] Löwenherz, *Ber.*, 25,1036 (1892).

2. The compound was readily resolved through the strychnine salt.

3. The active forms did not racemize under the ordinary conditions which might be expected to effect racemization.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE PREPARATION AND PROPERTIES OF CERTAIN SULFOXIDES AND SULFONES

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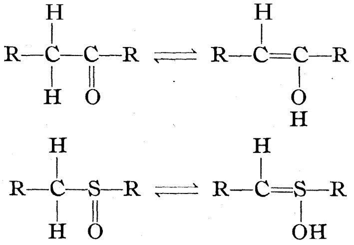
Although the enolization of a methylene group adjacent to a carbonyl group has been thoroughly studied, not much information is available on the behavior of compounds containing other linkages adjacent to a methylene group. The purpose of the present investigation was to study the influence exerted on a methylene group by the sulfoxide and sulfone linkages.

Using the customary notation, a comparison of the following formulas would indicate a similarity in chemical behavior; *i. e.*, under the proper conditions the sulfoxide might be expected to tautomerize in the same manner as the ketone



$$R-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{\|\\O}}{C}-R \rightleftharpoons R-\overset{\substack{H\\|}}{C}=\underset{\substack{|\\O\\H}}{C}-R$$

$$R-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{\|\\O}}{S}-R \rightleftharpoons R-\overset{\substack{H\\|}}{C}=\underset{\substack{|\\OH}}{S}-R$$

However, it has been known for some time that the chemical behavior of the sulfoxide linkage does not parallel that of the carbonyl.[1] Moreover, the electronic structures of sulfur–oxygen compounds, as formulated on the Lewis–Langmuir octet theory of valence, do not parallel exactly the electronic structure for carbon–oxygen.[2] The recent work of Sugden, who has found a considerable difference in the parachors of the carbonyl and the sulfoxide[3] groups, and the resolution by Phillips[4] of the sulfinic esters and sulfoxides, have furnished good evidence of the dis-

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[1] For example, the Grignard reagent does not add to the sulfoxide linkage as it does to the carbonyl linkage. Courtot, "Le Magnesium en Chimie organique," Rigot and Co., **1926**, pp. 125,225, ff.

[2] Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York, 1923, pp. 95,100.

[3] Sugden, *J. Chem. Soc.*, **125**, 1177 (1924); **127**, 1525, 1888 (1925).

[4] Phillips, *ibid.*, **127**, 2552 (1925); **129**, 2079 (1926).

similarity between these two groupings. The behavior of compounds containing the sulfone group adjacent to a methylene group has been studied in two instances. Michael and Comey[5] and Tröger and Lux[6] have prepared and studied benzene sulfonyl acetic ester, and Schroeder and Herzberg[7] have alkylated the esters of methionic acid. Although many of the simple sulfones of the type RSO_2R are described in the literature, practically no data are available on their properties and especially on the behavior of sulfones with different radicals.

Accordingly, a series of sulfoxides and sulfones was prepared, and their behavior toward reagents which would indicate the influence exerted by these groupings on the adjacent methylene groups studied. The compounds prepared are listed in Table I. They were made by modifications of general methods given in the literature which resulted in increased yields, and hence made larger quantities available for their study. The details of their preparation are given in the experimental part. Table I also lists the effect of various reagents on these sulfoxides and sulfones and summarizes the data obtained.

TABLE I

PROPERTIES OF SULFOXIDES AND SULFONES

Compound	Solubility in 10% NaOH	Solubility in 10% Na_2CO_3	Color with $FeCl_3$	Reaction metallic Na	Salt formation with sodium ethylate	Alkylation with MeI and NaOEt
Sulfoxides						
(1) $C_6H_5SOC_6H_5$	Insol.	Insol.	−	−	−	Not alkylated
(2) $C_6H_5SOCH_2C_6H_5$	Insol.	Insol.	−	−	−	Not alkylated
(3) $C_6H_5CH_2SOCH_2C_6H_5$	Insol.	Insol.	−	−	−	Not alkylated
(4) $C_6H_5SOCH_2SOC_6H_5$	Insol.	Insol.	−	−	−	Not alkylated
Sulfones						
(5) $C_6H_5SO_2CH_2C_6H_5$	Insol.	Insol.	−	+	+	Not alkylated
(6) $C_6H_5CH_2SO_2CH_2C_6H_5$	Sl. sol.	Insol.	−	+	+	Not alkylated
(7) $C_6H_5SO_2CH_2SO_2C_6H_5$	Sol.	Insol.	−	+	+	Gives mono and dimethyl alkylations

Theoretical Discussion

The Sulfoxides.—It will be noted that none of the methylene hydrogens in any of the sulfoxides (2, 3, 4) was activated. Diphenyl sulfoxide (1) was prepared and used as a control in order to guard against addition compounds. In each case the result was negative, even compound (4), which possessed a methylene group between two sulfoxide linkages, showed no tendency to alkylate and was recovered unchanged from the attempted alkylations. All of these compounds were insoluble in aqueous sodium and potassium hydroxides, and their benzene solutions did not

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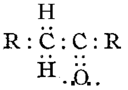
[5] Michael and Comey, *Am. Chem. J.*, 5, 116 (1883).

[6] Tröger and Lux, *Arch. Pharm.*, 247, 618 (1909).

[7] Schroeder and Herzberg, *Ber.*, 38, 3391 (1905).

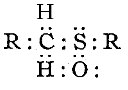
react with metallic sodium. Alcoholic solutions of these sulfoxides did not give any color with ferric chloride. The behavior of these sulfoxides is in sharp contrast to that of the corresponding ketones.

These results furnish further evidence that the nature of the sulfoxide linkage differs from that of the carbonyl. It is of interest in this connection to consider the following electronic formulas



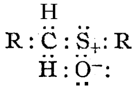
$$\begin{array}{cccc} & H & & \\ R: & \ddot{C} & :C: & R \\ & \ddot{H} & \cdot\ddot{O}\cdot & \end{array}$$

I



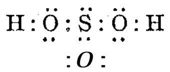
$$\begin{array}{cccc} & H & & \\ R: & \ddot{C} & :\ddot{S}: & R \\ & \ddot{H} & :\ddot{O}: & \end{array}$$

II



$$\begin{array}{cccc} & H & & \\ R: & \ddot{C} & :\ddot{S}_{+}: & R \\ & \ddot{H} & :\ddot{O}^{-}: & \end{array}$$

III



$$\begin{array}{c} H:\ddot{O}:\ddot{S}:\ddot{O}:H \\ :O: \end{array}$$

IV

Formulas II and III are the only ones possible which are consistent with the postulates of the octet theory[2] and Phillips'[4] resolution of the sulfoxides. Formula II is analogous to that given to sulfurous acid (IV) by Latimer and Rodebush[8] and used by them to explain the weakly acidic nature of sulfurous acid. Formula III is given by Sugden,[3] in which the sulfur–oxygen linkage is classed as a semi-polar linkage, *i.* e., a pair of electrons and an electrostatic charge.[9] Formulas II and III are essentially the same, the chief difference being one of notation. Latimer and Rodebush consider that the disproportionation of the electrostatic charges (caused by the fact that the oxygen is held to the sulfur atom by sharing only one pair of electrons, neither of which came from the oxygen atom) is understood as the natural result of writing Formula II. Sugden indicates this electrostatic effect at the sulfur-oxygen linkage in giving Formula[10] III.

In either case both Formulas II and III indicate a different condition of the oxygen atom from (I). It seems probable that it is the unshared pair of electrons on the sulfur atom which prevents the hydrogen atoms from ionizing. Latimer and Rodebush[8] explain the weakly acidic properties of sulfurous acid (IV) as due to the presence of an unshared pair of electrons on the sulfur atom. This mobile pair of electrons prevents the pulling in of the electrons shared between the oxygen and hydrogen in

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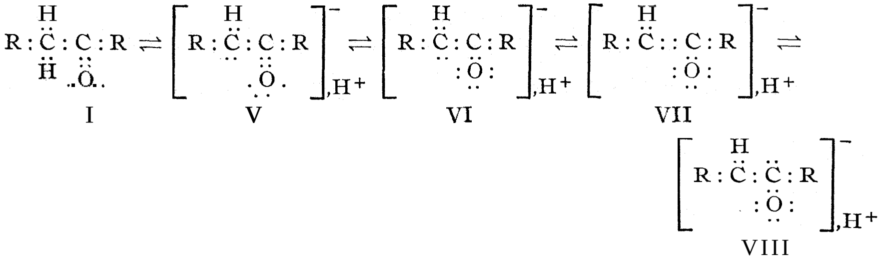
[8] Latimer and Rodebush, THIS JOURNAL, 42,1425 (1920).

[9] The disproportionation of the electrostatic charges can be shown by making use of the formula for the calculation of residual atomic charge. [See Langmuir, *Science*, 54, 59 (1921); Carothers, THIS JOURNAL, 46, 2228 (1924)]. Residual charge $= e - (S - V_e)$ where e is electrons in shell of the atom in free state; S is electrons in shell of the atom in the compound and V_e is valence. For the sulfur in a sulfoxide we obtain: Res. charge $= 6 - (8 - 3) = +1$. For the oxygen, Res. charge $= 6 - (8 - 1) = -1$. This, of course, is the fundamental basis for Sugden's formula.

[10] It is to be emphasized that Sugden's method of indicating the semi-polar double bond is a separate and distinct notation. The presence of the plus and minus signs does *not* indicate unit charges as in the case with H^+, Cl^- where there is the complete transference of an electron. It also has nothing in common with the use of plus and minus signs used by Fry, Lowry, Ingold and others to denote an alternating polarity.

the case of sulfurous acid and it seems probable that the same explanation will hold for the sulfoxide (II or III) where the unshared pair prevents the pulling in of the electrons between carbon and hydrogen.

Further support for this explanation may be obtained by considering the process of enolization of a ketone. In terms of the electron theory enolization may be regarded as a change from the non-polar form of (I) to the polar forms of (V, VI, VII, VIII), this transformation being due to the pull exerted by the oxygen atom on the electrons. These stages in the enolization of a carbonyl compound may be indicated as follows



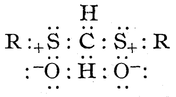
All four of the above polar forms are undoubtedly in equilibrium with each other and the electrostatic charges change from carbon to oxygen according to solvents and reagents.

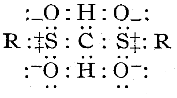
Now it is well known that only one of the hydrogens is tautomeric at a time; *i.* e., only one can be replaced by sodium and the second one does not ionize off or does so only to a very, very slight extent. The anions (V, VI, VII and VIII) would have to dissociate again and they exhibit no such tendency. Now these anions resemble, in one respect at least, the normal structure for the sulfoxides; i. e., there is present in (V, VI and VIII) an unshared pair of mobile electrons which act to prevent any further ionization of the second hydrogen atom of the adjacent carbon. Hence, in the sulfoxides which also possess an unshared pair of electrons (Formulas II, 111), the ionizing tendency should resemble the secondary ionization of (V, VI, VII, VIII); *i.* e., they should not undergo enolization. This is in agreement with the experimental data. It also receives confirmation from the data obtained on the corresponding sulfones.

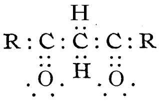
The Sulfones.—By reference to Table I it will be noted that the methylene hydrogens of the sulfones were activated in each case, the greatest activity being exhibited by Compound 7, which was readily soluble in sodium hydroxide and easily alkylated. The behavior of the sulfones is in sharp contrast to the behavior of the sulfoxides, which exhibited no such tendency. Dibenzoylmethane, which is the carbonyl compound analogous to methylene diphenyldisulfone, undergoes enolization[11] and may be alkylated but it is not soluble in aqueous alkalies. This behavior

[11] Claisen, *Ann.*, **277,** 184 (1893); **291,** 25 (1896).

constitutes still further evidence of the difference between the carbon–oxygen linkage and the sulfur–oxygen linkage. It is of interest to compare in this connection the electronic formulas for the sulfoxides, sulfones and carbonyl compounds

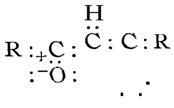

IX


X


XI

The first two formulas make use of the semi-polar linkage developed by Sugden as the result of the calculation of the parachors for sulfoxides and sulfones.[3] It has already been pointed out that the failure of the hydrogen of the methylene group in the sulfoxide (IX) to ionize was probably due to the presence of the unshared pair of electrons on the sulfur atom. The sulfone (X) contains no unshared pairs of electrons on its sulfur atoms. Each sulfur atom in the above sulfone has two semi-polar linkages, which results in the sulfur being doubly positive.[12] This resultant residual positive charge on the sulfur atom causes a distortion or pull on the electrons in the octet about the carbon of the methylene group which pulls in one pair of electrons and thus renders one of the hydrogens active. Since (X) has two sulfone groups, one on each side of the methylene group, the hydrogens in the latter group should be activated very readily. Compound 5 having only one sulfone group and a phenyl group about the methylene group should give rise to active hydrogens less readily and in dibenzyl sulfone (6) the distorting effect caused by the sulfonyl group is distributed among two methylene groups and hence this compound is the least active of the three.

The diketone (XI) contains a non-polar double bond on each of the carbons of the carbonyl group. The enolization of this substance is due to its transformation under the influence of reagents into one of the active forms of the double bond between carbon and oxygen.[13] If we suppose this conversion to result in the momentary production of the form shown, then it is evident that one carbonyl carbon carries a residual atomic charge of plus one and hence exerts a pull on the electrons of the octet about the methylene carbon atom with resultant activation of the hydrogen. Since the carbon in the above diketone carries a residual charge of only plus one, while the sulfur atoms in the disulfone (X) have a residual charge of plus two, it is now clear that the methylene hydrogens in (X) should be more active than those in (XI). This is in agreement with the experimental facts.



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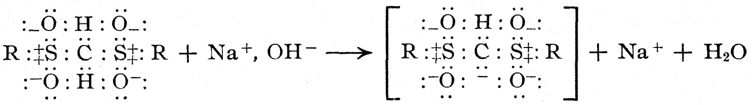
[12] *Cf.* Ref 9. The approximate residual charge calculated from the formula $e - (S - V_e)$, for the sulfur atom is $6 - (8 - 4) = +2$. This does not mean that there are two ***unit*** charges on the sulfur atom. See Ref. 10.

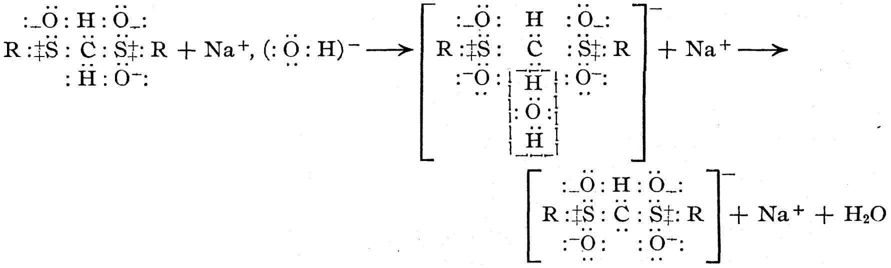
[13] Carothers, THIS JOURNAL, 46, 2229 (1924).

The conversion of the sulfone (X) into a salt under the influence of alkalies is of considerable theoretical interest since it is the first case in which the position of one of the residual negative charges is unquestionably on the methylene carbon atom.



It is obviously impossible to write any other electronic formula without violating the postulates of the octet theory. This, of course, does not mean that the sodium is attached to the carbon atom. This compound is an excellent example of the redistribution of electrostatic charges about the molecule in accordance with the reagents acting upon it. The second point of theoretical interest is that in the case of this sulfone the sodium salt is *not* formed as the result of a primary transformation to a true *enol* form,[14] with ionization of the enolic form, and finally combination of the hydrogen ion with the hydroxyl ion.

Since no true enol form exists, the formation of the sodium salt probably takes place by a combination of the sulfone with hydroxyl ion by means of a "bivalent" hydrogen[15] of the methylene group and subsequent elimination of a molecule of water. The following equation represents this type of transformation



Experimental

Preparation of Diphenyl Sulfoxide.—One hundred grams of benzene and 33 g. (0.28 mole) of thionyl chloride were placed in a 500-cc. round-bottomed flask. The

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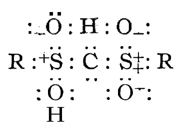
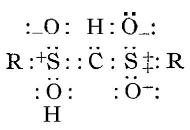
[14] The possibility of an enol form of either of the following forms is extremely improbable



A



B

Form (A) leaves an unshared pair of electrons on the central carbon and (B) puts ten electrons in the valence shell of sulfur.

[15] Lewis, "Valence arid the Structure of Atoms and Molecules," The Chemical Catalog Company, New York, 1923, p. 109.

mixture was immersed in an ice-salt bath and 60 g. of anhydrous aluminum chloride added in 0.5-g. portions over a period of two hours. Then 40 g. of benzene was added and the solution refluxed on a steam cone until no further hydrochloric acid gas was evolved.

After about one hour the contents were poured slowly on 600 g. of cracked ice which had been slightly acidified with dilute hydrochloric acid. A vigorous reaction took place and the yellow oil which separated was removed and washed four times with 50-cc. portions of distilled water. The excess benzene was driven off by distillation and the reddish-brown oil that remained solidified upon cooling. The diphenyl sulfoxide was extracted with (70-90") petroleum ether. Ten to fifteen extractions were necessary to completely remove the sulfoxide. It was a white crystalline substance, m. p. 70–71°, which agreed with the value given by previous investigators;[16] yield, 28.9 g. or 51%.

Anal. (Parr Bomb) Subs., 0.5158: $BaSO_4$, 0.5912. Calcd. for $C_{12}H_{10}SO$: S, 15.84. Found: S, 15.72.

Preparation of Dibenzyl Sulfide.[17]—One hundred and sixteen g. (0.56 mole) of benzyl chloride was dissolved in 300 cc. of 95% alcohol. The solution was then heated on the steam cone and 35 g. of sodium sulfide, which had been dissolved in 100 to 125 cc. of distilled water, was added. The mixture was stirred continuously and heated on the steam-bath for three days. The greater portion of the alcohol was distilled and the contents were then poured on 700 g. of cracked ice. The yellowish-brown oil which separated was removed and vacuum distilled to remove water and excess benzyl chloride. The distillation was accomplished by heating until the temperature of the vapors reached 134°, or until the distillate in the receiving flask began to solidify. The residual oil was then placed in the ice box until it solidified and was recrystallized from 70% alcohol; m. p. 49°; yield, 48 g. or 83%.

Preparation of Dibenzyl Sulfoxide.—Thirty grams of dibenzyl sulfide was dissolved in 250 cc. of acetone. The solution was filtered to remove undissolved substances. Then 15 g. of 30% hydrogen peroxide was added, the solution thoroughly shaken and allowed to stand at room temperature for forty-eight hours. The acetone was distilled and the oily residue cooled. It solidified to a white crystalline solid which was purified by recrystallization from petroleum ether;[18] m. p. 132–133°; yield, 22 g. or 75%.

Anal. Subs., 0.5463: $BaSO_4$, 0.5519. Calcd. for $C_{14}H_{14}SO$: S, 13.91. Found: S, 13.93.

Preparation of Benzyl Phenyl Sulfide.—Twelve grams (0.52 mole) of metallic sodium was dissolved in 300 cc. of absolute alcohol in a 1-liter three-necked flask fitted with a reflux condenser and a mechanical stirrer. Then 57 g. of thiophenol was added in a slow but steady stream. Next 68.8 g. of benzyl chloride was added drop by drop over a period of one and one-half hours and the mixture refluxed on a steam-bath for two hours. The alcohol was practically all distilled and while the solution was still hot it was poured on 400 g. of cracked ice. The impure sulfide was filtered and washed twice with 50-cc. portions of distilled water to remove any traces of sodium chloride. The sulfide was a white, crystalline compound;[19] m. p. 40–41°; yield, 61 g. or 60%.

Preparation of Benzyl Phenyl Sulfoxide.—Fifty-two grams of the sulfide was dissolved in 250 cc. of acetone. The solution was filtered to remove any undissolved substances. Then 40 g. of 30% hydrogen peroxide was added, the mixture thoroughly

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[16] Hinsberg, *Ber.*, 43, 289 (1910); Colby and McLaughlin, *ibid.*, 20, 195 (1887); Krafft and Lyons, *ibid.*, 29,441 (1896); Rosenheim and Singer, *ibid.*, 37,2154 (1904).

[17] Märcker, *Ann.*, 136, 90 (1865).

[18] Fromm aud Flaschen, *ibid.*, 394,310 (1912).

[19] Carlson, Ber., 40, 4194 (1907); Fromm, *ibid.*, 41, 3403 (1908).

shaken and allowed to stand at room temperature for seventy-two hours. The acetone was evaporated and the oil which remained solidified immediately upon slight cooling. The sulfoxide was recrystallized from 60% alcohol; m. p. 122–123°; yield, 40 g.

Anal. Subs., 0.4709: $BaSO_4$, 0.5105. Calcd. for $C_{13}H_{12}SO$: S, 14.81. Pound: S, 14.86.

Preparation of Methylene Diphenyl **Disulfide.**—This intermediate was prepared by modifying methods previously given by Otto and Tröger,[20] Baumann[21] and Fromm.[22] Twenty-three grams (1 mole) of metallic sodium was dissolved in 400 cc. of absolute alcohol. The mechanical stirrer was started and 110 g. (1 mole) of thiophenol was added in a slow but steady stream. Then 86.9 g. (0.5 mole) of methylene bromide was run in drop by drop. The addition of the methylene bromide took one hour. The mixture was refluxed, with stirring, on a steam-bath for two and one-half hours. The hot contents were immediately poured on 1000 g. of cracked ice. The solid product 'which separated was filtered and recrystallized from 95% alcohol. It was a white, crystalline powder; m. p. 35–36°; yield, 112 g. or 96.5%.

Anal. Subs., 0.3144: $BaSO_4$, 0.6294. Calcd. for $C_{13}H_{12}S_2$: S, 27.54. Found: S, 27.48.

Preparation of Methylene Diphenyl **Disulfoxide.**—Fifty grams of methylene diphenyl disulfide was dissolved in 400 cc. of acetone and filtered to remove any undissolved substances. Then 58 g. of 30% hydrogen peroxide was added. The mixture was allowed to stand at room temperature for forty-eight hours and heated for six hours at 37.5°. The acetone was distilled and the oil which remained behind was placed in the ice box overnight. The water was decanted and the solid disulfoxide was recrystallized five times from alcohol; m. p. 188–189°; yield, 30 g. or 52%.

Anal. Subs., 0.5004: $BaSO_4$, 0.8836. Calcd. for $C_{13}H_{12}S_2O_2$: S, 24.25. Found: S, 24.21.

Preparation of Phenyl Benzyl **Sulfone.**—Phenyl benzyl sulfone was prepared by the method given by Otto.[23] A mixture of 178 g. (1 mole) of sodium benzene sulfinate and 127 g. (1 mole) of benzyl chloride in 500 cc. of absolute alcohol was refluxed for seven to eight hours. The sulfinate did not dissolve completely, but this did not interfere with the reaction. The hot reaction mixture was poured into 1000 cc. of ice water. The crude product was filtered and dried. It was recrystallized from alcohol; m. p. 146–146.5°; yield, 120 g. (52%).

Anal. Subs., 0.5330: $BaSO_4$, 0.5363. Calcd. for $C_{13}H_{12}O_2S$: S, 13.78. Found: S, 13.80.

Preparation sf **Dibenzyl Sulfone.**—Twenty-five grams (0.11 mole) of dibenzyl sulfide was dissolved in 130 cc. of glacial acetic acid, and 32 g. of CrO_3 added over the period of an hour. The reaction was started by the application of heat, but, once started, it proceeded smoothly. After the CrO_3 was added, the mixture was refluxed gently for fifteen minutes. The hot solution was poured directly on 500 g. of crushed ice. The precipitate was filtered and washed with ice water. Recrystallization three times from 95% alcohol gave white needles; m. p. 149.5–150". This melting point agrees with that of Vogt and Henniger,[24] who prepared it by the action of benzyl chloride on potassium sulfite; yield, 7 g. or 23.7%.

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[20] Otto and Troger, *Ber.*, 25, 3429 (1892).

[21] Baumann, *ibid.*, 19,2806 (1886).

[22] Fromm, *Ann.*, 253, 161 (1889).

[23] Otto, *Ber.*, 21, 1696 (1888).

[24] Vogt and Henniger, *Ann.*, 165,375 (1873).

Anal. Subs., 0.5255: $BaSO_4$, 0.4979. Calcd. for $C_{14}H_{14}O_2S$: S, 13.00. Found: S, 13.00.

Preparation of Methylene Diphenyl Disulfone.—A modification of the methods of Otto and Tröger[20] and Fromm[22] was used; 18 g. (0.077 mole) of crude methylene diphenyl disulfide was dissolved in 80–100 cc. of glacial acetic acid and 42 g. of CrO_3 was added slowly over a period of one and one-half hours. The flask was warmed at first, but later the reaction proceeded smoothly without further heating. After the reaction had stopped, the hot mixture was poured on 1000 g. of crushed ice. The crude methylene diphenyl disulfone was filtered by suction and washed with ice water. Recrystallization twice from water gave white needles; yield, 4.2 g. (18% of the theoretical); m. p. 118–119°.

Anal. Subs., 0.4888: $BaSO_4$, 0.7640. Calcd. for $C_{13}H_{12}O_4S_2$: S, 21.62. Found: S. 21.48.

Properties of Sulfoxides

I. Solubility in Alkali.—The solubilities of the above four sulfoxides in 5 and 10% sodium and potassium hydroxides were tested. None of the compounds dissolved.

II. Metallic Sodium.—A solution of 0.5 g. of each of the above sulfoxides in dry benzene was treated with 0.1 g. of sliced sodium. No reaction took place in the cold.

III. Ferric Chloride.—Addition of ferric chloride to alcohol solutions of these sulfoxides caused no deepening of the yellow color as compared with a blank alcohol solution.

IV. Attempted Alkylations.—All three of the above sulfoxides were treated with sodium ethylate in absolute alcohol and methyl iodide added. A typical experiment is as follows.

Attempt to Alkylate Methylene Diphenyl Disulfoxide.—Eighty-seven hundredths gram of metallic sodium was dissolved in 100 cc. of absolute alcohol and 10 g. of methylene diphenyl disulfoxide was added. The solution was heated to dissolve the disulfoxide and 17 g. of methyl iodide was added slowly over a period of fifteen minutes with vigorous shaking. The mixture was then refluxed on a steam-bath for three hours and the hot contents poured on 200 g. of cracked ice. The reddish-brown solid upon recrystallization was found to be the original compound; m. p. 188–189°.

Properties of Sulfones

I. Solubility in Dilute Alkalies.—The solubilities of the three sulfones in 10% sodium and potassium hydroxides were tested. It was found that methylene diphenyl disulfone dissolved readily, phenyl benzyl sulfone only partially and dibenzyl sulfone not at all. All of the sulfones were completely insoluble in 6 N hydrochloric acid and this reagent was used to precipitate the first two compounds above from their alkaline solutions. All of the sulfones were insoluble in 5 and 10% sodium carbonate solution.

II. Metallic Sodium.—A solution of 0.5 g. of each of the above sulfones in dry benzene was treated with 0.1 g. of sliced sodium. Hydrogen was liberated very slowly and the sodium became coated with the salt after about half an hour.

III. Ferric Chloride.—Addition of dilute ferric chloride to alcohol solutions of these sulfones caused no deepening of the yellow color as compared with a blank alcohol solution.

IV. Alkylations.—The alkylation of phenyl benzyl sulfone and dibenzyl sulfone was attempted using the same procedure outlined above. Both compounds failed to alkylate and were recovered almost quantitatively from the reaction mixture unchanged.

Alkylation of Methylene Diphenyl Disulfone

(a) With One Equivalent of Methyl Iodide.—To a solution of 0.23 g. (0.01 mole) of sodium in 300 cc. of absolute alcohol was added 3 g. (0.01 mole) of methylene diphenyl disulfone. Next, 1 cc. (slight excess) of methyl iodide was added and the mixture refluxed for two and one-half hours; 150–200 cc. of alcohol was distilled from the mixture and the residue poured on crushed ice. The precipitate was filtered by suction and washed with ice water. Four recrystallizations from alcohol gave white needles: yield, 1 g. (47.6%); m. p. 100–101"; mixed melting point with original disulfone (m. p. 118–119°), 80–86°; mixed melting point with disubstitution product (m. p. 181–182°), 94–98°.

Anal Subs., 0.2821: $BaSO_4$, 0.4151. Calcd. for $C_{14}H_{14}O_4S_2$: S, 20.64. Found: S, 20.22.

(b) With Two Equivalents of Methyl **Iodide.**—To a solution of 0.46 g. (0.02 mole) of sodium in 300 cc. of absolute alcohol was added **3** g. (0.01 mole) of methylene diphenyl disulfone. Next, ***2.5*** cc. (slight excess) of methyl iodide was added and the mixture refluxed for two and one-quarter hours; 150 cc. of alcohol was distilled from the flask and the residue poured on crushed ice. The product was filtered bv suction and washed with ice water. Three recrystallizations from alcohol gave white needles: m. p. 181–182°; mixed melting point with original disulfone (m. p. 118–119°), 101–105°.

Anal. Subs., 0.4672: $BaSO_4$, 0.6723. Calcd for $C_{15}H_{16}O_4S_2$: S, 19.75. Found: S, 19.76.

Summary

1. The preparation and enolization tendency of certain sulfoxides have been studied. It was found that the sulfoxides do not tautomerize into enolic forms under the conditions used.
2. Phenyl benzyl sulfone, dibenzyl sulfone and methylene diphenyl disulfone were prepared and their properties studied.
3. The hydrogen of the methylene group in methylene diphenyl disulfone was most active and the hydrogen in dibenzyl sulfone least active.
4. In each case the sulfone group activated the hydrogens to a much greater extent than the sulfoxide group.
5. Some of the theoretical aspects of the behavior of these compounds are discussed.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

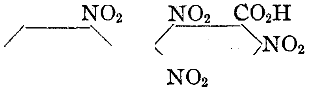
STEREOCHEMISTRY OF DIPHENYL COMPOUNDS. VI. PREPARATION AND RESOLUTION OF 2,4,6,2′,4′-PENTANITRO-3-CARBOXYDIPHENYL[1]

BY H. A. STEARNS[2] AND ROGER ADAMS

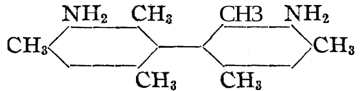
RECEIVED JANUARY 21, 1930 PUBLISHED MAY 8, 1930

Only two 2,2′,6-trisubstituted derivatives of diphenyl have as yet been prepared and resolved. Both of these compounds were readily racemized in alkaline solution. Pertinent information concerning the phenomenon of optical activity in the diphenyl series should be obtained more readily by a study of 2,2′,6-trisubstituted compounds than from the 2,2′,6,6′-tetrasubstituted compounds.

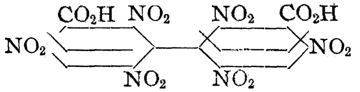
In this communication is given the description of 2,4,6,2′,4′-pentanitro-3-carboxydiphenyl (I), the first trisubstituted derivative prepared with the 2,2′,6-positions filled with the same groups and with each of the rings unsymmetrical in itself. As might be anticipated after the preparation and resolution of 2,2′,6,6′-tetramethyl-3,3′-diaminodiphenyl (II) and 2,4,6,2′,4′,6′-hexanitro-3,3′-dicarboxydiphenyl (111), this trisubstituted compound was readily resolved. Further evidence is thus submitted that the mechanical interference of the groups is preventing free rotation of the rings.



I



II



III

The active forms of 2,4,6,2′,4′-pentanitro-3-carboxydiphenyl are stable to racemization. Eight hours of boiling in ammonium carbonate solution or six hours of boiling in glacial acetic acid, or several days' standing in cold sodium carbonate solution failed to change the rotation, and eight hours of boiling in 95% acetic acid saturated with hydrogen chloride failed to change the rotation more than slightly. Hot sodium carbonate solution caused a deep reddening of the solution so that possible racemization could not be determined.

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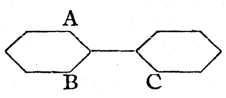
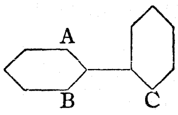
[1] For previous papers in this field see (a) Hyde and Adams, THIS JOURNAL, 50, 2499 (1928); (b) Moyer and Adams, *ibid.*, 51, 630 (1929); (c) Stanley and Adams, *Rec. trav. chim.*, 48, 1035 (1929); (d) This JOURNAL, 52, 1200 (1930); (e) Bock, Moyer and Adams, *ibid.*, 52, 2054 (1930).

[2] This communication is a portion of an abstract of a thesis submitted by H. A. Stearns in partial fulfilment of the requirement for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

The probable effects within these trisubstituted molecules should be considered. If it is assumed that the two rings remain symmetrically placed toward each other when they arrive in or approach the same plane, then all that should be required for a substance to be capable of resolution is to have in the general formula (IV), group C large enough to interfere materially with B and with A.



IV



V

If the interference at either or both points is small, the compound should racemize more or less readily. If, however, the two rings may be assumed to bend toward each other when the same plane for both rings is approached closely (in the manner represented in V), it is conceivable that non-resolution of certain compounds which should otherwise be capable of resolution might be expected. Though during the process of resolution much distortion of this kind seems unlikely, it might well occur under the conditions used in racemization experiments and consequently racemization of certain compounds might readily take place.

A 2,2′,6-trinitro compound from this standpoint would give the following results. Using the values[1d] $\mathrm{C{-}NO_2}$, 1.92 Å; C–H, 0.92 Å.; C–C (2,2′), 2.90 Å, the interference of two nitro groups will be as follows: 1.92 Å. + 1.92 Å. = 3.84 Å. − 2.90 Å. ⟶ + 0.94 Å., a large difference compared to what was found necessary for interference in the tetrasubstituted compounds. At the same time on the other side of the molecule the nitro and the hydrogen would not collide at all; 1.92 Å. + 0.92 Å. = 2.84 Å. − 2.90 Å. ⟶ −0.06 Å. If the molecules were distorted so that the nitro and the hydrogen pulled toward each other more than 0.06 Å., collisions would occur on both sides of the molecule simultaneously, without reducing to any great extent the interference between the two nitro groups. In such a molecule racemization would not be expected and does not occur.

On the other hand, such a compound as 2,6-diamino-2′-methyldiphenyl presents other possibilities. Using the values, $\mathrm{C{-}NH_2}$, 1.56 Å.; $\mathrm{C{-}CH_3}$, 1.73 Å.; C–H, 0.92 Å., on the side of the molecule holding the amino and methyl groups the interference would be as follows: 1.73 Å. + 1.56 Å. = 3.29 Å. − 2.90 Å. ⟶ +0.39 Å. On the other side of the molecule 1.56 Å. + 0.92 Å. = 2.48 Å. − 2.90 Å. ⟶ −0.42 Å. Upon the assumption of a symmetrical position for the two rings at all times, resolution of the compound should take place readily and the active compounds should not racemize at all or at least not readily. On the other hand, if the amino and the hydrogen are pulled toward each other to the extent of 0.39 Å., then the groups could pass by each other without collisions on either side of the molecule. Although it is improbable that such a distorted position would exist so as to prevent resolution, it is likely that under certain conditions it might be approached to an extent which would allow easy racemization of the active compounds. The extent to which the possible distortion might occur in various molecules will, of course, depend upon the character of the groups present. It is of little value to speculate further with the x-ray data until more facts are available.

In connection with the assumptions just made, it is necessary to consider the 2,4′-dinitro-6,6′-dicarboxydiphenyl[3] and the 2,4,4′-trinitro-6,6′-dicarboxydiphenyl,[4] both of which have two carboxyls and one nitro group in the critical positions. Using the values given previously and in addition C–COOH, 1.56 Å., the side with two carboxyls would give the following results: 1.56 Å. + 1.56 Å. = 3.12 Å. − 2.90 Å. ⟶ +0.22 Å. On the other side, 1.92 Å. + 0.92 Å. = 2.84 Å. − 2.90 Å. ⟶ −0.06 Å. It is obvious, then, that not much distortion would be necessary in such a molecule to reduce the interference to the point where racemization would take place. These substances do racemize slowly by heating at 100° with sulfuric acid. On the other hand, if the size of the carboxyl groups is decreased, as happens when ionized, racemization should be comparatively rapid. Results have shown these compounds to racemize readily in alkaline solution.

The 2,4,6,2′,4′-pentanitro-3-carboxydiphenyl was prepared by condensing, under carefully specified conditions, 2,4,6-trinitro-3-bromotoluene and 2,4-dinitrochlorobenzene by means of copper. The resulting compound, 2,4,6,2′,4′-pentanitro-3-methyldiphenyl was oxidized with a mixture of fuming nitric acid, fuming sulfuric acid and sodium dichromate to the corresponding carboxylic acid. This latter compound was resolved readily through the strychnine salt.

Experimental

2,4,6,2′,4′-Pentanitro-3-methyldiphenyl.—In a 1-liter flask equipped with a mechanical stirrer were placed 133 g. of 2,4-dinitrochlorobenzene, 100 g. of 2,4,6-trinitro-3-bromotoluene,[5] 240 cc. of nitrobenzene and 3 g. of copper bronze. The mixture was stirred and heated on an oil-bath until the contents of the flask had reached a temperature of 160°, at which temperature brown copper halides began to form. The oil-bath was then removed, and 230 g. of copper bronze was added at such a rate that the reaction mixture remained at a temperature of 160–165° during the addition. Exterior heating was then continued so that the mixture remained within this temperature range for a total period of one hour.

The hot reaction mixture was filtered, the copper residues extracted with acetone and the extract added to the filtrate. Acetone and nitrobenzene were then removed from the products by means of a steam distillation. The product was next washed with

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[3] Christie and Kenner, *J. Chem. Soc.*, **121**, 614 (1922); 470, 671 (1926).

[4] Kuhn and Albrecht, *Ann.*, 455, 272 (1927); 458, 221 (1927).

[5] Bentley and Warren, *Am. Chem. J.*, **12**, 4 (1890).

alcohol to remove traces of nitrobenzene, dissolved in acetone and this solution refluxed with norite for one-half hour. After filtration, the acetone was evaporated off and the residue washed twice with alcohol, then recrystallized from glacial acetic acid until a melting point of 200–201° was reached. Finally, the product was dissolved in a minimum of boiling acetone, and thrown out of solution as a fine, white, granular powder by the addition of a large excess of alcohol; melting point, 200–201°. The yield was about 52 g. (40%).

Anal. Calcd. for $C_{13}H_7O_{10}N_5$: C, 39.69; H, 1.80. Found: C, 39.74; H, 2.08.

2,4,6,2′,4′-Pentanitro-3-carboxydiphenyl.—In a 1-liter flask provided with a mechanical stirrer and cooled by means of a salt–ice-bath was placed 20 g. of pure 2,4,6,2′,4′-pentanitro-3-methyldiphenyl dissolved in 220 cc. of fuming nitric acid[6] (sp. gr. 1.52). Eighty cubic centimeters of fuming sulfuric acid (20%) was added to the stirred mixture at such a rate that the temperature did not rise above 20° during the addition. To the stirred and cooled solution, 40.4 g. of powdered potassium dichromate was added at such a rate that the temperature of the solution did not rise above 10° during the addition (about three-quarters of an hour). Stirring was continued for twenty-four hours, and the bath was permitted to rise slowly to room temperature during this period. The reaction mixture was then poured into a large excess of ice and the free acid obtained by filtration. The acid was purified by recrystallization from benzene and formed a fine, white, crystalline powder of m. p. 205–206°. The yield was 7 g. (32.5%).

The yield from this reaction varied from 30 to 50% for successive runs, apparently because of a difference in purity of the crude acid obtained. The crude acid varies considerably in purity depending upon conditions which have not been defined. If, upon one crystallization from benzene, the melting point of the crude acid rises, further recrystallization will readily purify it; on the other hand, if the melting point lowers or if, for any other reason, the acid acts peculiarly, it is advisable to purify through the pyridine salt. This was precipitated from a saturated alcoholic solution of the acid by the slow addition of its chemical equivalent of pyridine. The salt was extracted twice with small amounts of boiling benzene, then dissolved in a minimum of acetone, and the free acid obtained by the addition of excess concentrated hydrochloric acid to this solution. The acetone solution was cooled and stirred during the hydrochloric acid addition, and the acid so obtained was recrystallized from benzene.

Anal. Calcd. for $C_{13}H_5O_{12}N_5$: C, 36.88; H, 1.19; N, 16.55. Found: C, 36.98; H, 1.83; N, 16.88.

Resolution of 2,4,6,2′,4′-Pentanitro-3-carboxydiphenyl.—To a solution of 10.2 g. of 2,4,6,2′,4′-pentanitro-3-carboxydiphenyl in 700 cc. of methyl alcohol was added slowly and with stirring 800 cc. of a solution of 8.08 g. of strychnine in 2 liters of methyl alcohol. The solution was cooled to 0° and allowed to stand for one hour. A crop (7.5 g.) of pale yellow, needle-like crystals (A) was obtained. To the mother liquor from (A) was added an additional 300-cc. portion of the strychnine–methyl alcohol solution. The resulting mixture was evaporated to about 700 cc. under diminished pressure and a second crop (3 g.) of yellow crystals (B) was filtered off. To the mother liquor from (B) was added the remainder of the strychnine solution. This mixture was evaporated to a volume of about 300 cc., cooled overnight at 0°, and a third crop (7.8 g.) of orange-colored, granular crystals (C) obtained.

Crystals (A) were purified by dissolving them in a minimum of warm acetone and adding to this stirred solution petroleum ether until the solution was slightly opaque. Upon standing overnight at 0°, the salt separated as fine, pale yellow needles. The

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[6] A good grade of fuming nitric acid is important. Inferior grades give much poorer results.

purified salt turns red at 265° and melts with decomposition at some point between 270 and 280°. Two successive recrystallizations of salt **(A)** sufficed to bring the salt to a constant rotation.

Rotation. 0.1373 g. of salt made up to 15 cc. with pyridine at 20° gave om $-1.13°$; $l = 1$, $[\alpha]^{20}_{D}$ $-123.5°$.

Anal. Calcd. for $C_{34}H_{27}O_{14}N_7$: C, 53.88; H, 3.59. Found: C, 53.75; H, 4.06.

Strychnine salt (C) was purified by dissolving it in boiling alcohol, evaporating this solution down to such a volume that crystals started to appear in the hot solution, then allowing the solution to stand at 0° overnight. Crystals of (C) were obtained as a light orange colored powder. This material turns red at 203–205° and apparently melts at 222–226°. Two successive recrystallizations brought the rotation to a constant value.

Rotation. 0.1319 g. made up to 15 cc. in pyridine at 20° gave α_D $+0.74°$, $l = 1$, $[\alpha]^{20}_{D}$ $+84.4°$.

Anal. Calcd. for $C_{34}H_{27}O_{14}N_7$: C, 53.88; H, 3.59. Found: C, 53.52; H, 4.35.

l-2,4,6,2′,4′-Pentanitro-3-carboxydiphenyl.—To 2.19 g. of the pure strychnine salt **(A)** was added 20 cc. of acetone. Solution was not complete. The beaker was cooled with an ice-bath, and 50 cc. of concentrated hydrochloric acid added with stirring, at such a rate that the temperature of the mixture was always kept below 20°. The cooled mixture was permitted to stand for fifteen minutes so as to assure complete crystallization of the free acid, then filtered. The acid was completely redissolved in 10 cc. of acetone and again thrown out of solution by the addition of 50 cc. of concentrated hydrochloric acid in the manner just described. The acid was dried *in vacuo* at room temperature and then purified further by recrystallizing twice from benzene to a constant rotation and melting point. The pure acid was obtained as white, granular crystals of melting point 233". The yield was 0.87 g. (71.3%).

Rotation. 0.1165 g. of acid made up to 15 cc. in acetone at 20° gave α_D $-0.82°$, $l = 1$, $[\alpha]^{20}_{D}$ $-105.3'$.

d-2,4,6,2′,4′-Pentanitro-3-carboxydiphenyl.—To 1.19 g. of the strychnine salt (C) dissolved in 5 cc. of acetone and cooled with an ice-bath, slowly and with stirring was added 50 cc. of concentrated hydrochloric acid. The cooled mixture was permitted to stand for one-half hour so as to assure complete crystallization of the liberated acid, then filtered. The acid was redissolved in 9 cc. of acetone and reprecipitated by the addition of another 50-cc. portion of concentrated hydrochloric acid in the manner just described. It was recrystallized twice from benzene and formed a white, granular powder of melting point 229–231°. It gave a negative strychnine test when dissolved in sulfuric acid and treated with manganese dioxide. The yield of recrystallized acid was 0.4 g.

Rotation. 0.1116 g. of acid made up to 15 cc. in acetone at 20° gave α_D $+0.73$, $l = 1$, $[\alpha]^{20}_{D}$ $+98.8°$.

Racemization Experiments

(a) **A** 0.1357-g. sample of d-2,4,6,2′,4′-pentanitro-3-carboxydiphenyl was made up to 25 cc. in glacial acetic acid at 20° and the following rotation found for the solution: α_D $+0.53$, 1 = 1, $[\alpha]^{20}_{D}$ $+98.3°$. The entire solution was transferred to a ***50-cc.*** flask equipped with a glass-fitted reflux condenser and refluxed for one and one-half hours. The solution was then evaporated to a volume of about 10 cc., transferred to a volumetric flask, and its volume again made up to 25 cc. with glacial acetic acid at 20°. The rotation of the solution was then α_D $+0.53°$; *1* = 1, $[\alpha]^{20}_{D}$ $+98.3'$. The solution was refluxed for an additional two and one-half hours and its rotation again taken: cuD $+0.52°$, $l = 1$, $[\alpha]^{20}_{D}$ $+95.8°$.

(b) **A** 0.1268-g. sample of l-2,4,6,2′,4′-pentanitro-3-carboxydiphenyl, $[\alpha]^{20}_{D}$ -105.3" in acetone, was refluxed with 20 cc. of 5% ammonium carbonate solution for a period of eight hours. The solution was then cooled with an ice-bath and 30 cc. of concentrated hydrochloric acid added slowly and with stirring. The precipitated acid was filtered from this mixture, dried *in vacuo* at room temperature, and its rotation taken as follows: 0.1073 g. of acid made up to 15 cc. in acetone at 20° gave α_D $-0.76°$, $l = 1$, $[\alpha]^{20}_D$ $-105.8°$.

(c) A 0.1236-g. sample of the *l*-acid, $[\alpha]^{20}_D$ $-105.3°$ in acetone, was dissolved in 20 cc. of a solution that had been prepared by saturating an acetic acid solution, which contained 5% of water, with hydrogen chloride. The resulting solution was refluxed for eight hours, then cooled in an ice-bath and 50 cc. of concentrated hydrochloric acid added. After permitting the cooled mixture to stand for one-half hour. the precipitated acid was filtered from it, dried *in vacuo* at room temperature, and its rotation taken as follows: 0.0967 g. of acid made up to 15 cc. in acetone at 20° gave α_D $-0.54°$, $l = 1$, $[\alpha]^{20}_D$ $-83.4°$.

(d) A 0.1535-g. sample of the *l*-acid was made up to 15 cc. in a 5% sodium carbonate solution at 20° and its rotation taken: α_D $-2.13°$, $l = 1$, $[\alpha]^{20}_D$ $-208.0°$. This pale yellow solution was permitted to stand in a sealed tube at room temperature for seven days, during which period it developed an amber color. Its rotation was then taken and found to be: α_D $-2.11°$, $l = 1$, $[\alpha]^{20}_D$ $-206.3°$.

An attempt was made to heat the solution in a sealed tube to a temperature of 50–60°, but after eight hours of this treatment the solution had developed such a deep red color that its rotation could not be taken.

Summary

1. The compound 2,4,6,2′,4′-pentanitro-3-carboxydiphenyl has been prepared and resolved. This is the first diphenyl derivative with three of the same groups in the 2,2′,6-positions which has been resolved.

2. The active forms could not be racemized in acid, neutral or alkaline solution.

3. Discussion is given of what properties may be anticipated of various 2,2′,6-trisubstituted diphenyls.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT OHIO STATE UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. IV. 4-METHYL-4-OCTENE BY ISOPRENE ETHYLATION

BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

RECEIVED JANUARY 22, 1930 PUBLISHED MAY 8, 1930

In preceding papers[1] it has been shown that when isoprene accepts hydrogen, or when two molecules of isoprene link together, the reaction affects only the 1- and 4-positions. This behavior has been regarded as a general property, and it has been used to explain the polymerization of isoprene to synthetic rubber.

The present paper offers one more evidence of the 1,4-addition. Two ethyl groups have been attached to an isoprene molecule

$$H_2C{=}C(CH_3)CH{=}CH_2 + 2C_2H_5Br \xrightarrow{Na} CH_3CH_2CH_2C(CH_3){=}CHCH_2CH_2CH_3$$

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[1] Midgley and Henne, THIS JOURNAL, 51, 1215, 1293, 1294 (1929).

The experimental conditions were precisely those which are required for the formation of synthetic rubber: the reaction took place at room temperature in the presence of an alkaline metal and, in each case, a certain amount of synthetic rubber was formed. This favors the view that the ethylation of isoprene is a process very analogous to its polymerization.

As was expected, the ethyl groups linked exclusively to the first and the fourth carbon atoms; a hydrocarbon was thus obtained which on examination proved to be 4-methyl-4-octene. The criteria used for its identification were a combustion, a molecular weight determination by freezing point depression in benzene, a double bond determination by hydrogenation and by bromination, a computation of the molecular refraction and finally an oxidation with ozone.

Since the experimental results support the postulation that isoprene accepts radicals *exclusively* on its 1- and 4-carbon atoms (under the conditions required for synthetic rubber formation), they also fortify the hypothesis that the chain formula of natural rubber proposed by Staudinger[2] and his associates is much more acceptable than any formula involving the formation of a ring.

Experimental

Two-gram molecules of metallic potassium are covered with one gram molecule of isoprene, which has been sufficiently purified to be capable of rapid polymerization. Two-gram molecules of ethyl bromide (or one gram molecule of ethyl sulfate) is dissolved in a like volume of dry ether, and added gradually to the isoprene. A gentle shaking is maintained, and heat is applied sufficiently to maintain a moderate ebullition. Much gas is evolved; the decomposition of the ethylation agent is the predominant reaction. After twenty-four hours, the residual metal is eliminated by the cautious addition of alcohol, and the ethylate is then decomposed with water. The mixture is washed with dilute hydrochloric acid and water, decanted, dried and fractionated. About 4% of the theoretical amount of C_9H_{18} is obtained. This compound shows the following physical constants: b. p. 136–144° (chiefly 139°), d_{20}^{20} 0.7495, n_D^{20} 1.4225, A = 1.0 per C_9H_{18}. The molecular weight determined by freezing point depression in benzene was found to be 122: theory requires 126, but the discrepancy is within the permissible experimental error of 3%. A combustion checked the formula already evident. The molecular refraction computed from the density and the refractive index by means of the Lorentz–Lorenz formula was found to be 42.8. This value compares favorably with the theoretical value 43.3.

To prove that isoprene had accepted the ethyl groups exclusively on the 1- and 4-carbon atoms, it was necessary to locate the double bond in the resulting nonene, and this was done by ozone oxidation in a glacial acetic acid solution. The ozonization procedure has been previously recommended.[3] After decomposition of the ozonide with a dilute potassium dichromate solution, two compounds were isolated and characterized: methyl butyl ketone, and butyric acid. No trace of any other compound was detected. The results of the ozonization were in complete agreement with the formula postulated for the nonene.

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[2] Staudinger and co-workers, *Helv. Chim. Acta*, 5,785 (1922), and later papers.

[3] Henne, THIS JOURNAL, 51, 2676 (1929).

Summary

Isoprene has been ethylated; 4-methyl-4-octene was formed exclusively. The structure of this nonene is in agreement with the usual behavior of a conjugated double bond system. This type of addition is further evidence in favor of the hypothesis which regards the polymerization of isoprene to synthetic rubber as the formation of long chains of isoprene units linked together by ordinary valences in the 1,4-position.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT OHIO STATE UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. V. TETRAMETHYLOCTADIENE

BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

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The third paper of this series[1] has shown how the polymerization of isoprene to synthetic rubber could be stopped at the dimeric stage by addition of an atom of hydrogen to each terminal carbon of the transitory dimer.

A similar experiment can be carried out with dimethylbutadiene substituted for isoprene. Although details differ, the general trend of the reaction remains the same, the reaction products are comparable and the conclusions are similar.

If the views presented before are correct, the linkage of two molecules of dimethylbutadiene, during polymerization to methyl-rubber, should form the transitory compound

$$—H_2CC(CH_3)=C(CH_3)CH_2CH_2C(CH_3)=C(CH_3)CH_2—$$

Should polymerization be allowed to proceed further, the unstable molecules would link together by their terminal free valences and form a long chain; methyl-rubber would be the final product. This agrees with Kondakow's ideas.[2] On the other hand, should polymerization be stopped by addition of an atom of hydrogen on each end of the unstable dimeric derivative, a duodecadienic hydrocarbon should result. This hydrocarbon has been isolated and analyzed. As expected, it was 2,3,6,7-tetramethyl-2,6-octadiene.

The polymerization of dimethylbutadiene can never be entirely stopped at the dimeric stage; an appreciable amount of a rubber-like material is always formed. The amount of this compound varies with the experimental conditions. This can be used as an evidence that the formation of tetramethyloctadiene and that of methyl-rubber are simultaneous and

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[1] Midgley and Henne, THIS JOURNAL, 51, 1294 (1929).

[2] I. L. Kondakow, "Scientific Memoirs of the Imperial Yuriev University for the year 1901."

analogous processes. Consequently, the structure of the tetramethyloctadiene will have a very close relation to the structure of methyl-rubber. Moreover, since isoprene and dimethylbutadiene behave in a similar way, the structure of ordinary synthetic rubber may be postulated by analogy with that of methyl-rubber.

Experimental

The apparatus, procedure and proportions of reagents have been described previously. Runs were made at 0, 25 and 70°. In each case, 200 g. of dimethylbutadiene has been used. The best yield was obtained by running at 70°; 65 g. of $C_{12}H_{22}$ was collected and 45 g. of C_6H_{10} recovered, the balance being polymerized to methyl-rubber (15 g.) or carried out with the escaping hydrogen. The tetramethyloctadiene, purified by fractionation under reduced pressure, exhibited the following constants: b. p. (18 mm.) 87.5–88.5°, d_4^{25} 0.7971, n_D^{25} 1.45963. Molecular refraction found, 57.0; calcd., 56.7. The determination of the number of double bonds was made by bromination with a KBr–$KBrO_3$ mixture, and by hydrogenation in the presence of platinum oxide; in each case 4 atoms were accepted per molecule of hydrocarbon. To complete the analysis, a combustion, a molecular weight determination by freezing point lowering in benzene and an oxidation with ozone were performed. The ozonization was carried out in glacial acetic acid, as reported previously.[3] Two compounds were obtained and characterized: acetone and acetonylacetone. Not a trace of any other derivative could be detected. The result of the examination thus proves that the formula of the tetramethyloctadiene is $(CH_3)_2C{=}C(CH_3)CH_2CH_2(CH_3){=}C(CH_3)_2$.

The physical constants of the compound obtained by hydrogenation have been measured. They are: b. p. (20–22 mm.) 92°, d_4^{25} 0.7593, n_D^{25} 1.42527; mol. refr, found, 57.2; calcd., 57.6. A combustion and a molecular weight determination agree with the expected values. From its method of formation this compound should be 2,3,6,7-tetramethyloctane.

It is to be noted that when the polymerization is carried out at a low temperature the sample of tetramethyloctadiene obtained is considerably less pure; its boiling point is not constant, it can be fractioned into portions whose densities and refractive indexes vary between d_4^{25} 0.7980 and 0.8003 and n_D^{25} 1.45952 and 1.46111. The odor of the compound strongly resembles that of turpentine. Particularly, the addition of bromine or hydrogen to the double bonds is strongly hampered. This gave the impression that only one double bond was present and led to the erroneous belief that a ring compound had been formed. A better interpretation would be to consider that tetramethyloctadiene formed at low temperature is contaminated by a small quantity of cyclic or even dicyclic compound, which would account for the odor, the higher density and the high refractive index.

Summary

Dimethylbutadiene treated with potassium and alcohol gives 2,3,6,7-tetramethyl-2,6-octadiene and methyl-rubber. The structure of the first hydrocarbon has been established, and is used as an evidence that the methyl-rubber formula must be a long, open chain. This is also regarded as an evidence in favor of the chain formula of natural rubber.

COLUMBUS, OHIO

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[3] Midgley and Henne, THIS JOURNAL, 51, 2676 (1929).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE PREPARATION AND PROPERTIES OF SOME NEW FURAN DERIVATIVES[1]

BY FREDUS N. PETERS, JR., AND RICHARD FISCHER

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Forty-six years ago Pawlinoff and Wagner[2] prepared ethyl furyl carbinol, the first known alkyl furyl carbinol, from furfural and zinc diethyl. In 1901, Grignard[3] obtained iso-amyl furyl carbinol by the use of furfural and iso-amylmagnesium halide. During the same year Hale, McNally and Pater[4] reported negative results in their attempt to obtain phenyl furyl carbinol from the reaction between furfural and phenylmagnesium halide and a similar failure has been reported by Mahood and Jordan.[5] While the manuscript from which this paper is abstracted was being prepared, Pierce and Adams[6] reported the preparation of crude phenyl furyl carbinol and of n-butyl furyl carbinol and ethyl furyl carbinol, the latter compound having previously been prepared by Douris.[7] Jolkver[8] and Jaworsky[9] prepared n-propyl and allyl furyl carbinol, respectively.

This paper describes the preparation and properties of several heretofore unreported alkyl furyl carbinols, impure phenyl furyl carbinol, several esters of these substances and a few unidentified oxidation and chlorination products.

The organomagnesium furyl complexes obtained in the preparation of these carbinols by the Grignard reaction are pale to orange-yellow in color and, with one exception, insoluble in ether. The exception is the n-butyl derivative, which in this respect is similar to titanium n-butoxide, which is also an ether-soluble substance, while the lower aliphatic titanium alkoxides are ether insoluble. Isobutylfurylmagnesium bromide was obtained more nearly white than any of the other insoluble magnesium furyl complexes.

All of the carbinols are colorless liquids when pure. They are slightly soluble in water, the solubility and density decreasing with increasing molecular weight. They are all completely miscible with alcohol, nitro-

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[1] This paper is part of a dissertation presented in 1925 by Fredus N. Peters, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] Pawlinoff and Wagner, *Ber.*, 17, 1967 (1884).

[3] Grignard, ***Ann. chim. phys.***, [7] 24, 468 (1901).

[4] Hale, McNally and Pater, ***Am. Chem.*** J., **35,** 68 (1901).

[5] Mahood and Jordan, ***Science,*** 60,453 (1924).

[6] Pierce and Adams, THIS JOURNAL, 47, 1098 (1925).

[7] Douris, ***Compt. rend.,*** 157, 722 (1923).

[8] Jolkver, ***Rec. trav. chim.,*** 28,439 (1909).

[9] Jaworsky, ***Ber.,*** 42,435 (1909).

benzene, benzene, chloroform and ether. Phosphorus pentachloride, acetyl chloride, benzoyl chloride and concentrated hydrochloric acid resinify the carbinols, the first two reagents acting with almost explosive violence. Light and air change the carbinols more or less rapidly to reddish brown, viscous liquids which solidify upon standing for some time. Treatment with metallic sodium liberates hydrogen and produces a dark brown mass, soluble in alcohol or ether. The methyl and phenyl furyl carbinols are the most unstable toward acids, whereas the isopropyl furyl carbinol is practically unchanged within two hours by 10% hydrochloric acid and when the pure substance is sealed in a glass tube it remains colorless for several months. Methyl furyl carbinol in a sealed tube in an atmosphere of hydrogen was only slightly colored within one year and after four years it has changed very little more. The other alcohols which were less carefully protected became dark brown liquids in this time. The alkyl furyl carbinols have very little odor and none that can be ascribed as distinctly due to the furan nucleus, the odor being dependent more on the nature of the radical attached to the secondary carbon atom.

The preparation of the esters was not attempted in every case but where tried the only successful method was the treatment of an ethereal solution of the carbinol with acetic anhydride using anhydrous sodium acetate as a catalyst. This method did not give results with the methyl and phenyl derivatives, these being resinified by even small quantities of acetic acid. Treatment of the magnesium complex of furfural and ethyl bromide with acetyl chloride or with benzoyl chloride resulted in resinification of the substance within one hour. The magnesium complex was also treated with ethyl acetate according to the method of Stadnikoff.[10] However, nothing but ethyl acetate and the unchanged carbinol were isolated at the close of the experiment. The use of pyridine according to the method of Einhorn also failed to produce an ester of methyl furyl carbinol. Attempts to prepare an ester of ethyl furyl carbinol by the Schotten–Baumann or Einhorn methods failed. Pawlinoff reported failure in attempts to prepare this ester.

Molecular refractions were calculated using the values for atomic refractions given by Roth and Eisenlohr[11] and in every case checked very well with the values obtained from the Lorentz–Lorenz formula. Molecular weights were determined cryoscopically using benzene as a solvent.

It was impossible to prepare phenyl furyl carbinol in a pure state, the product always being contaminated with diphenyl and some unidentified products. Attempts to oxidize n-butyl furyl carbinol with potassium permanganate in acid solution gave a colorless liquid, b. p. 90–95° (3 mm.),

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[10] Stadnikoff, *Ber.*, 57, 1 (1924).

[11] Roth and Eisenlohr, "Refraktometrisches Hilfsbuch," Veit and Co., Leipzig, 1911, p. 128.

insoluble in **10%** hydrochloric acid or sodium hydroxide. This product was slightly acidic and slowly decolorized bromine water; it gave no phenyl hydrazone, semicarbazide or sodium bisulfite addition products. This material resinified to a yellow, viscous gel within one week.

Treatment of ethyl furyl carbinol with diethyl sulfate and potassium hydroxide gave no appreciable yield of the expected ether. The product obtained by treating ethyl furyl carbinol with metallic sodium was refluxed with ethyl bromide and a small quantity of material of aromatic odor was isolated but the amount was too small for characterization. Dry hydrochloric acid gas diluted with carbon dioxide was passed through an ethereal solution of n-butyl furyl carbinol. A liquid, b. p. 90–95° (5 mm.), containing chlorine was isolated. This chloride upon refluxing with sodium ethoxide precipitated sodium chloride and a small quantity of liquid with a pronounced terpene-like odor was obtained.

Experimental

Reagents.—The furfural used in this work was obtained through the courtesy of The Miner Laboratories of Chicago, to whom the authors are deeply grateful. The magnesium employed was in the form of turnings furnished for this purpose. The ether and organic halides were dried and purified by conventional methods.

TABLE I

SECONDARY ALCOHOLS, $C_4H_3OCH(OH)R$

R	Yield, %	Boiling points, °C.		n^{25}_{25}		
				D	C	F
Methyl	67	76–77 (23 mm.)	1.0771	1 4785	1.4751	1.4874
Ethyl	82	57–8 (6 mm.), 89–90 (23 mm.), 106–107 (55 mm.), 113 (71 mm.), 120 (95 mm.)	1.0474*	1.4759*	1.4724*	1.4877*
n-Propyl	55	76–77 (5 mm), 84–5 (9 mm.), 91–2 (12 mm.)	1 0179	1 4768	1.4727	1.4862
Isopropyl	75	99–100 (38 mm.)	1.0111	1.4715	1.4680	14800
n-Butyl	72	94–6 (2 mm.)	0 9931	1 4710	1 4675	1 4788
Isobutyl	40	102–3 (10 mm.)	0.9904	1 4687	1 4646	1 4762
Phenyl	26	122–5 (2 mm.), 138–42 (10 mm.), 170–180 (39 mm.) decompn.	1 1423	1 5522	....	....

* Temperature, 20°

R	Formula	Carbon, %			Hydrogen, %			R_m	
		Calcd.	Found		Calcd.	Found		Calcd.	Found
Methyl	$C_6H_8O_2$	64.26	64.51	64.55	7.21	7.05	7.01	29.94	29.48
Ethyl	$C_7H_{10}O_2$	66.62	66.36	66.37	7.99	7.71	7.71	34.56	34.00
n-Propyl[a]	$C_8H_{12}O_2$	68.53	68.96	68.64	8.63	8.66		39.18	38.88
Isopropyl	$C_8H_{12}O_2$	68.53	68.63	68.34	8.63	8.50	8.43	39.18	38.77
n-Butyl	$C_9H_{14}O_2$	70.09	70.12		9.15	9.11		43.80	43.37
Isobutyl	$C_9H_{14}O_2$	70.09	70.13		9.15	8.94	8.99	43.80	43.32
Phenyl[b]	$C_{11}H_{10}O_2$	75.83	76.59	76.69	5.79	6.14	6.08	49.43	48.71

[a] Mol. wt., calcd., 140; found, 146. [b] Mol. wt., calcd., 174; found, 191, 189.

TABLE II

ALKYL FURFURYL ACETATES, $C_4H_3OCRH(OOC{-}CH_3)$

R	Yield, %	Boiling points, °C.	d^{25}_{25}	n^{25}_{25} D	C	F
Ethyl	40	98 (37 mm.), 102–3 (40 mm.)	1.0427[a]	1.4589	1.4552	1.4662
Isopropyl	67	99–100 (35 mm.)	1.0162	1.4641	1.4606	1.4712
Isobutyl	35	119–20 (30 mm.)	1.0004	1.4600	1.4556	1.4664

[a] Temperature, 26°.

R	Formula	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found		Rm Calcd.	Rm Found
Ethyl	$C_9H_{12}O_3$	64.24	64.41	64.23	7.20	7.00	6.98	43.81	44.29
Isopropyl	$C_{10}H_{14}O_3$	65.90	65.72	65.86	7.75	8.20	8.02	48.43	49.46
Isobutyl	$C_{11}H_{16}O_3$	67.29	67.44	67.55	8 22	8.08	8.15	53.04	53.70

Procedure.—In the early work a special apparatus was used in which the organomagnesium halide was formed in a dry, carbon dioxide–oxygen-free atmosphere and then was forced through a glass wool filter into the furfural. The majority of experiments, however, were carried out by forming the Grignard reagent in the usual manner and adding the furfural to the cool and well-stirred solution. Approximately one gram mole of the Grignard reagent was used in each run. Hydrolysis was carried out by pouring the mixture over ice and this was followed by steam distillation without the use of ammonium chloride or other reagent generally added to aid hydrolysis. The distillate was treated with solid potassium carbonate and the organic layer was shaken with freshly prepared bisulfite solution to remove any unreacted furfural. This was followed by treatment with sodium carbonate to neutralize any free acid and then by vacuum distillation.

Tables I and II give the compounds isolated and some of their physical constants.

Summary

1. Methyl, ethyl, propyl, isopropyl, butyl, isobutyl and phenyl furyl carbinols have been described and some of their physical and chemical properties reported.
2. The acetic acid esters of ethyl furyl, isopropyl furyl and isobutyl furyl carbinols have been prepared and some of their physical properties determined.
3. A chloride, which is probably *α-n*-butyl furfuryl chloride and two substances which are very likely the ethyl ethers of ethyl and n-butyl furyl carbinols, respectively, were isolated.
4. An unidentified product was isolated from the acid permanganate oxidation of n-butyl furyl carbinol.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS AND THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

THE SIMPLE HALOGEN DERIVATIVES OF FURAN

BY A. F. SHEPARD, N. R. WINSLOW AND JOHN R. JOHNSON

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Syntheses in the furan series are limited by the lack of direct methods for introducing organic radicals into the furan ring. For this reason the furan derivatives which have been most widely studied are largely those with substituent organic groups in the 2-position, for which furfural serves as a suitable starting material. A certain number of furan derivatives with organic substituents in the 2- and 5-positions are available from 5-methylfurfural and its derivatives,[1] and a few others may be obtained through various types of ring formation that lead to furan derivatives.[2]

3-Methylfuran[3] and 3-furoic acid[4] have been obtained from natural sources but the structure of these compounds has not been confirmed by synthesis. In fact, a review of the literature showed that no furan derivative with a single organic substituent in the 3-position has ever been synthesized. Although halogen, nitro and sulfonic acid groups may be introduced directly into the furan ring, the resulting compounds have not been studied further with the idea of introducing organic substituents by indirect methods. With the object of extending the methods of synthesis in the furan series through the use of these groups, a series of investigations was undertaken. The present paper deals with the preparation and properties of the simpler halogen derivatives of furan.

Although a number of halogenated furans containing two or more halogen atoms are known,[5] only one of the monohalogenated furans, 3-bromofuran,[6]

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[1] The synthesis of furan derivatives with a methyl group in the 5-position and substituent groups in the 2-position has been facilitated by the recent observation that certain replacement reactions of α-furfuryl chloride involve rearrangement of the α-furfuryl group into the 5-methyl-2-furyl group [Runde, Scott and Johnson, THIS JOURNAL, 52, 1284 (1930); Reichstein, Ber., **63**, 749 (1930)].

[2] An excellent review of this subject is given by Marquis, *Ann. chim. phys.*, [8] *4*, 200–208 (1905); see also Benary, *Ber.*, 44, 493 (1911).

[3] Asahina and Tanaka [*Acta Phytochim.*, 2, 1 (1924); C. A., 19, 1139 (1925)] prepared 3-methylfuran by decarboxylation of 3-methyl-2-furoic acid, which had been obtained from the naturally occurring ketone, elscholtzione.

[4] Rogerson, *J. Chem. Soc.*, 101, 1044 (1912); Power and Salway, *Pharm. J.*, 90, 550 (1913); C. A., 7, 2659 (1913).

[5] These include 2,5- and 3,4-dibromofuran, 2,5-di-iodofuran, 2,3,4-tribromofuran, 2,3,4-tribromo-5-chlorofuran, tetrabromofuran and tetra-iodofuran.

[6] Canzoneri and Oliveri, *Gazz. chim. ital*, 17, 43 (1887). These authors obtained a small amount of 3-bromofuran in an attempt to prepare 3-hydroxyfuran or 3-hydroxyfuroic acid by heating 3-bromofuroic acid with excess calcium hydroxide. Although they stated an intention of preparing an hydroxyfuran from this compound and of preparing the isomeric 2-bromofuran, we were unable to find any further published results on this subject.

has been obtained in a state of purity. Several investigators have noted the formation of these compounds in small amounts but have not purified or characterized them.[7]

For the purpose of preparing the simple halogenated furans it appeared that the corresponding furoic acids would be the most satisfactory materials. Various chlorofuroic and bromofuroic acids have been prepared in a pure state by Hill and his collaborators,[8] and the positions of the halogens have been established with reasonable certainty. By decarboxylation of these acids, the corresponding halogenated furans of known constitution could be obtained. After a preliminary study it was found that this method was quite satisfactory and the chlorofurans and bromofurans could be obtained in excellent yields.

Decarboxylation of 3-broniofuroic acid, 5-bromofuroic acid, 3,4-dichlorofuroic acid and 3,4,5-trichlorofuroic acid was effected simply by heating the substances at temperatures between 210 and 300°. 3-Chlorofuroic acid and 5-chlorofuroic acid proved to be more stable and could not be decarboxylated in this way. It was found that copper bronze or finely divided nickel, prepared by reducing the oxide at 300–400°, effectively catalyzed the decarboxylation[9] and in the presence of these catalysts 3-chlorofuroic acid and 5-chlorofuroic acid could be decarboxylated. The results of typical decarboxylation experiments are given in Table I.

It seemed likely that the pyrolysis of the halogenated furoic acids under the above conditions gave rise through secondary reactions to the formation of some free halogen acid, toward which the simpler furan derivatives are relatively sensitive. In order to avoid decomposition of the resulting halogenated furans, it appeared advisable to effect the decarboxylation in the presence of a base, which would combine with any free halogen acid formed during the pyrolysis. Quinoline was selected as a suitable base and proved to be quite satisfactory. The addition of quinoline made possible the isolation of 2-bromofuran, which we had not been able to accomplish in earlier experiments, and effected a marked improvement in the yields in other cases. The results of a series of semi-quantitative

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[7] (a) Henninger [*Ann. chim. phys.*, [6] 7, 222 (1886)] states that the bromination of furan leads to a monobromofuran and a dibromofuran, but describes only the latter. (b) Hill and Jackson [*Proc. Am. Acad. Arts Sci.*, 24, 320 (1888)] state that a small amount of a colorless liquid separated upon adding water to the first portions of the distillate obtained upon distilling the alcoholic alkali used in saponifying ethyl 5-chlorofuroate. This liquid, which they did not investigate lurther, may have been a monochlorofuran or a dichlorofuran.

[8] (a) Hill and Sanger, *ibid.*, 21, 135 (1885); (b) Hill and Hartshorn, *Ber.*, 18, 448 (1885); (c) Hill and Palmer, *Proc. Am. Acad. Arts Sci.*, 23, 188 (1887); (d) Hill and Jackson, *ibid.*, 24, 320 (1888); (e) Hill and Hendrixon, *ibid.*, 25, 283 (1889); (f) Hill and Wheeler, *Am. Chem. J.*, 25, 463 (1901).

[9] Sabatier, "Catalysis in Organic Chemistry," translated by E. Emmet Reid, D. Van Nostrand and Co., New York, 1922, par. 831–839.

TABLE I

PYROLYSIS OF HALOGENATED FUROIC ACIDS

Substituted furoic acid	Decompn. temp. (approx.), °C.	Sample, g	Substituted furan	Product, g	Yield, %
3-Chloro-	260[a]	20	3-Chloro-	4.2	30
5-Chloro-	260[a]	20	2-Chloro-	6.7	47
3,4-Dichloro-	300	20	3,4-Dichloro-	9.6	63
3-Bromo-	260	20	3-Bromo-	7.4	48
5-Bromo-	210	20	2-Bromo-	0[b]	0

[a] One gram of copper bronze (Kahlbaum's "Naturkupfer C") was added in these experiments, since these acids did not decompose appreciably below 300° in the absence of catalysts.

[b] 5-Bromofuroic acid was readily decarboxylated but the resulting 2-bromofuran was converted into a black resin in the reaction tube. The resinification of the product was circumvented in later experiments (see Table II) and yields of 2-bromofuran as high as 90% of the theoretical were obtained.

experiments, in which the evolved carbon dioxide was measured, are shown in Table II.

TABLE II

PYROLYSIS OF HALOGENATED FUROIC ACIDS IN THE PRESENCE OF COPPER BRONZE AND QUINOLINE

Substituted furoic acid	Temp.,[a] °C.	Sample, g.	Carbon dioxide Found	Carbon dioxide Calcd.	Carbon dioxide Percentage of calcd.	Substituted furan	Percentage of theory[b]
3-Chloro-	250	5.00	1.45	1.50	96	3-Chloro-	79
5-Chloro-	240	10.00	3.19	3.01	106	2-Chloro-	91
3,4-Dichloro-	220	10.00	2.46	2.43	101	3,4-Dichloro-	97
5-Bromo-	220	15.00	3.38	3.45	98	2-Bromo-	75

[a] This column indicates the minimum temperature of the bath which was necessary to obtain vigorous decomposition. The acids decomposed slowly at somewhat lower temperatures.

[b] The yields given here are based upon the weights of the products after purification by two steam distillations.

The monohalogen derivatives of furan are colorless liquids with a pleasant sweet odor closely resembling that of chloroform and bromoform. With strong aqueous hydrochloric acid they produce at first a green coloration, and on longer standing change to resins. 3,4-Dichlorofuran does not give this coloration with hydrochloric acid, but forms a resin on standing in contact with this reagent. The halogen atoms in these compounds are surprisingly unreactive; all attempts to carry out metathetical reactions were entirely unsuccessful. Such reagents as aqueous sodium hydroxide and sodium cyanide solutions, metallic sodium, mercury dimethyl and zinc dimethyl were without action.[10] In one case, however, it was possible to obtain a Grignard reagent. 2-Bromofuran in ethereal solu-

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[10] Several of the experiments mentioned here were carried out by Mr. E. B. Reinbold, who also found that the bromine atom of ethyl 5-bromofuroate was extremely unreactive.

tion, on treatment with a highly activated magnesium–copper alloy,[11] gave 2-furylmagnesium bromide. The latter was characterized by the formation of 2-furoic acid by the action of carbon dioxide, and of 2-furoic anilide by the action of phenyl isocyanate. The use of this Grignard reagent in synthesis should render available a number of furan derivatives that cannot be prepared by the usual methods, such as difurylcarbinol, trifurylcarbinol, and others.

Experimental Part

Preparation of Halogenated Furoic Acids.—The methods used for the preparation of the various halogenated acids were essentially those of Hill and his collaborators,[8] with slight modifications in a few details. The acids used in this work were free from isomeric acids according to the criteria of Hill, and their purity was checked by halogen determinations.

Substituted furoic acid	*M. p., °C. (corr.)*	*Percentage of halogen*[a]		
		Calcd.	*Found*	
3-Chloro-	148.5–149.5	Cl, 24.20	24.04	23.99
5-Chloro-	179–180	Cl, 24.20	24.29	23.90
3,4-Dichloro-	169.5–170.5	Cl, 39.19	39.00	38.33
3,4,5-Trichloro-	174.5–175.5	Cl, 49.39	48.97	48.73
3-Bromo-[c]	127–129	Br, 41.85	......[c]	
5-Bromo-	184–186	Br, 41.85	40.87[b]	

[a] Halogen determinations by the Parr peroxide bomb method.

[b] 5-Bromofuroic acid was purified conveniently as the ethyl ester, which was readily prepared through the acid chloride. The latter method was more satisfactory than direct esterification with ethyl alcohol and sulfuric acid. Forty-eight grams (0.25 mole) of 5-bromofuroic acid was heated for one and one-half hours with 57 g. (0.275 mole) of phosphorus pentachloride, and part of the resulting oxychloride was removed by distillation from an oil-bath at 125–130°. The residue was treated cautiously with 100 cc. of absolute alcohol and warmed for three or four hours. The crude ester was washed with a large volume of water, then sodium bicarbonate solution, dried and distilled. There was obtained 48 g. (87% yield) of ethyl 5-bromofuroate, b. p. 134–136° at 34 mm. (Br analysis, calcd., Br, 36.51. Found: Br, 36.62, 36.85). Similarly, 3,4-dichlorofuroic acid gave ethyl 3,4-dichlorofuroate in 90% yield.

[c] For our first experiments on the preparation of 3-bromofuran we used pure 3-bromofuroic acid, m. p. 127–129°, which was obtained according to Hill's procedure by the reduction of 3,5-dibromofuroic acid, prepared by the bromination of furoic acid. In later experiments in an attempt to improve the preparation of 3,5-dibromofuroic acid, we brominated furoyl chloride and obtained a dibromofuroic acid which was apparently not pure 3,5-dibromofuroic acid. The dibromofuroic acid from furoyl chloride gave on reduction a monobromofuroic acid or a mixture of monobromofuroic acids which melted indefinitely at 110–118° instead of 128–129°. Bromine determinations and neutralization values showed that the material in hand corresponded to a monobromofuroic acid or a mixture of monobromofuroic acids (Br: calcd., 41.25; found, 41.60; neutralization value: calcd., 190.9; found, 191.3, 192.9), and decarboxylation gave 3-bromofuran. It appears that bromination of furoyl chloride gives rise to a mixture of 3,5-dibromofuroic acid and 4,5-dibromofuroic acid. Reduction of

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[11] Gilman, Peterson and Schulze, ***Rec. trav. chim.***, 47, 19 (1928).

these would produce 3-bromofuroic acid and 4-bromofuroic acid, both of which would yield 3-bromofuran on decarboxylation. Since Hill and his collaborators have not described 4-bromofuroic acid or 4,5-dibromofuroic acid, further work is being done to determine the nature of the products of bromination of furoyl chloride and of the monobromofuroic acid obtained therefrom.

Preparation of Halogenated **Furans.** General Procedure.—Decarboxylation of the halogenated furoic acids was carried out by heating the acids in a large pyrex tube, 25 × 200 mm., bearing a side tube which was provided with a small condenser and a receiver for the liquid distillate. The decomposition tube was closed with a cork holding a glass tube drawn out to a narrow tip reaching to within 60–80 mm. of the bottom of the tube. Dry nitrogen was passed through the small tube to provide an inert atmosphere and to remove the volatile products as rapidly as possible from the zone of high temperature. The decomposition tube was heated in a bath of Wood's metal at temperatures varying from 210–300° (see Tables I and II). It was found that better yields were obtained by decomposing the acids in small portions of about 5 g. each.

Five grams of the halogenated furoic acid, 10 g. of quinoline and 1 g. of copper bronze (Kahlbaum's "Naturkupfer C") were placed in the reaction tube, which was lowered into a previously heated bath of Wood's metal. The bath was maintained at such a temperature that a vigorous evolution of carbon dioxide took place. The decarboxylation proceeded smoothly and the halogenated furan distilled into the receiving flask. When the acid was completely decarboxylated, as shown by cessation of gas evolution, the tube was raised from the bath and allowed to cool. A second portion of 5 g. of the halogenated acid was added and the above process repeated. In this way 20–30 g. of the acid could be decarboxylated before dismantling the apparatus. In cases where the decomposition temperature of the halogenated furoic acid was relatively high, it proved advantageous to use a base of higher boiling point than quinoline (b. p. 238°) in order to avoid distilling traces of the base into the receiving flask. For this purpose a high-boiling fraction of crude coal tar bases, b. p. 285–310°, proved entirely satisfactory.[12] The halogenated furans were purified by two steam distillations and were dried over fresh calcium oxide. After trial experiments had shown that these substances did not react with metallic sodium, certain of them were dried by means of this metal, *e. g.*, 3-chlorofuran and 2-bromofuran. The yields of the halogenated furans varied from 75–95% of the calculated amounts

The halogenated furans are slightly soluble in water and soluble in organic solvents such as alcohol, ether and benzene; they have an odor very similar to that of chloroform or bromoform. The purified products were colorless liquids when freshly distilled but darkened on standing and eventually changed completely to insoluble resins.[13]

It was found that the products could be kept for months without appreciable decomposition by covering them with an alkaline solution of hydroquinone and storing in corked bottles. Determinations of physical constants were made on freshly distilled specimens of the pure liquids boiling over less than 0.5° temperature range, and samples for analysis were sealed in small bulbs within thirty minutes of the time of distillation. Halogen determinations were made by the Parr bomb method on samples sealed in thin-walled glass bulbs.[14] The physical constants and analyses of the halogenated furans are shown in Tables III and IV.

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[12] The authors wish to express their thanks to Mr. W. R. Gerges of the Chemical Department of the Barrett Company, Philadelphia, for supplying a generous sample of this material.

[13] Compare Moureu, Dufraisse and Johnson, *Ann. chim.*, [10] 7, 28 (footnote) (1927).

[14] Lemp and Broderson, THIS JOURNAL, 39, 2069 (1917).

TABLE III

PHYSICAL CONSTANTS OF HALOGENATED FURANS

Halogenated furan	Boiling point, °C. Temp. (corr.)	Press. mm.	d^{20}_{4}	n^{20}_{D}	Molecular refraction[a] Obs.	Calcd.	MR_D (obs.) − MR_D (calcd.)
2-Chloro-	77.2–77.5	744	1.1923	1.45687	23.40	24.05	−0.65
3-Chloro-	79.0–79.4	742	1.2094	1.46005	23.21	24.05	−0.84
3,4-Dichloro-[b]	122.8–123.1	744	1.4136	1.48612	27.82	28.92	−1.10
2,3,4-Trichloro-	151.7–152.7	734	1.5471	1.5057	32.90	33.78	−0.88
2-Bromo-	101.9–102.2	744	1.6500	1.49805	26.11	26.95	−0.84
3-Bromo-[c]	102.5–102.6	745	1.6606	1.49575	25.84	26.95	−1.11

[a] The molecular refractions of these compounds were calculated frpm the revised values of Eisenlohr for the atomic refractions [Landolt-Bornstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 5th ed., Vol. II, 1923, p. 985]. The observed molecular refractions were calculated by the Lorentz–Lorenz formula.

[b] 3,4-Dichlorofuran solidified when cooled in an ice-bath, and the m. p. was found to be 3.8–4.0° (corr.) with the thermometer immersed in the liquid.

[c] Other physical constants of 3-bromofuran are: b. p. 50° at 110 mm., 38.5" at 40 mm.; d^{0}_{0} 1.6957; n^{20}_{C} 1.49185.

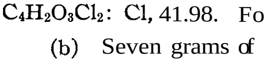
TABLE IV

ANALYSIS OF HALOGENATED FURANS

Halogenated furan	Carbon, % Calcd.	Found		Hydrogen, % Calcd.	Found		Halogen, % Calcd.		Found	
2-Chloro-	46.84	46.95	46.70	2.95	3.00	2.90	Cl	34.60	34.48	34.41
3-Chloro-	46.84	47.17	47.01	2.95	2.95	2.97	Cl	34.60	34.54	34.52
3,4-Dichloro-	35.05	34.86	34.84	1.47	1.52	1.46	Cl	51.79	51.61	51.68
2,3,4-Trichloro-	...	...	...	..	..	..	Cl	62.08	61.60"	61.56
2-Bromo-	32.67	32.62	32.76	2.06	2.06	2.10	Br	54.39	54.41	54.48
3-Bromo-	...	...	...	..	..	..	Br	54.39	53.15[b]	53.48

[a] The combustion analyses of this compound were unsatisfactory, probably on account of the difficulty of achieving complete combustion and complete retention of the halogen.

[b] Analysis for bromine in this particular compound was effected by the method of Stepanow [*Ber.*, 39, 4056 (1906)] and the low results are probably due to loss of bromofuran by volatilization. The Stepanow method for halogen determinations was replaced by the Parr bomb method for all other compounds, but the analyses of 3-bromofuran were not repeated since this compound had previously been described and analyzed.

Oxidation of **3,4-Dichlorofuran.**—(a) Ten grams of pure 3,4-dichlorofuran was added slowly to 28 g. of nitric acid (sp. gr. 1.42) at room temperature. The oxidation proceeded slowly at first and then became extremely vigorous. On standing the solution deposited crystals, which were filtered and crystallized from hot water. After drying in a vacuum desiccator the product weighed 3 g.; m. p. 124–125° (corr.). The melting point and chlorine analysis indicate that this compound is mucochloric acid,  $\underbrace{HO—CH—CCl=CCl—CO}_{O}$, (α,β-dichloro-β-formylacrylic acid).

Anal. Subs., 0.1792, 0.2966: 20.60, 34.20 cc. of 0.1018 *N* $AgNO_3$. Calcd. for $C_4H_2O_3Cl_2$: Cl, 41.98. Found: Cl, 41.50, 41.62.

(b) Seven grams of pure 3,4-dichlorofuran was added slowly to 21 g. of fuming nitric acid (sp. gr. 1.49) at room temperature. A transient green coloration was developed and oxides of nitrogen were evolved in large quantity. After standing for two days the crystals that had separated were filtered, pressed on a porous plate and dried in a vacuum desiccator. The crude dichloromaleic anhydride weighed 5 g. and melted at 110–115°; it was identified by the procedure of Salmony and Simonis,[15] by heating with aniline. The resulting anil of anilidochloromaleic anhydride, after crystallization from alcohol, formed greenish-yellow crystals, which discolored on heating and melted to a brown liquid at 188.7–190.2° (corr.). Salmony and Simonis reported that the anil of anilidochloromaleic anhydride began to turn brown at 175° and melted to a brown liquid at 188°.

Attempt to Prepare **2-Iodofuran.**—A number of experiments were made in an effort to prepare a mono-mercurated furan, from which an iodofuran might be obtained by treatment with iodine in aqueous potassium iodide. Ciusa and Grillo[16] succeeded in obtaining tetrachloromercuri-furan and in converting it to tetra-iodofuran by this method. In one experiment they obtained a mono-mercurated furan but were unable to repeat this preparation, and were consequently unable to obtain a mono-iodofuran. In our experiments we used a mixture of mercuration products and attempted to separate the mixture of iodo derivatives obtained therefrom. The following experiment illustrates the methods used.

A solution of 318 g. of mercuric acetate in 1300 cc. of water was added slowly, while stirring vigorously, to a solution of 150 g. of furoic acid in 2 liters of water at 80°. Bubbles of carbon dioxide were evolved and a heavy precipitate was formed. After standing for twelve to twenty-four hours to complete the reaction, the precipitate was filtered with suction and washed thoroughly with water. To convert the mercuri-acetate to the corresponding mercuri-chloride, the moist precipitate was stirred with a solution of 75 g. of sodium chloride in 1 liter of water, and allowed to stand for thirty minutes. The resulting precipitate was filtered with suction, suspended in 4–5 liters of water, and treated dropwise with a solution of iodine in aqueous potassium iodide, until a faint color indicated the presence of an excess of iodine. The amount of iodine added corresponded to 0.80–0.85 mole for each mole of furoic acid used. The resulting suspension was extracted several times with ether and, after drying and distilling off the solvent, a semi-solid residue remained. In a preliminary experiment, when this material was distilled through a fractionating column, a small amount of liquid distilled at 120–125°; the temperature then rose sharply and the residue decomposed rapidly with the evolution of violet vapors. For this reason, in subsequent experiments the residual mixture of iodofurans was subjected to three or four steam distillations in order to effect a partial separation of the liquid products from the solids. In this way there was obtained 3 g. of a liquid fraction (sp. gr. > 1) which was dried over anhydrous sodium sulfate and distilled at atmospheric pressure. About 2 g. of an almost colorless liquid, with an odor resembling that of iodoform, distilled at 120–140°. Since the liquid acquired a green color very rapidly, samples were sealed at once for analysis. Within thirty minutes of the time of distillation both the sealed samples and the material that had been allowed to stand in the air had completely resinified. For this reason the halogen determinations were not satisfactory.

Anal. Subs., 0.2978, 0.2054: 15.70, 9.10 cc. of 0.1018 N $AgNO_3$. Calcd. for C_4H_3OI: I, 65.5. Found: I, 68.11, 57.37.

2-Furylmagnesium Bromide.—Preliminary experiments indicated that 2-bromofuran in ethereal solution did not react with ordinary magnesium nor with magnesium activated by heating with iodine. It was found, however, that 2-bromofuran would react with a magnesium–copper alloy[17] that had been activated by heating with half

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[15] Salmony and Simonis, ***Ber.***, 38, 2588 (1905).

[16] Ciusa and Grillo, *Gazz. chim. ital.*, *57*, 323 (1927).

its weight of iodine. In solution in di-n-butyl ether[17] no reaction occurred with the activated magnesium-copper alloy, even on heating to 100°.

A solution of 8 g. of 2-bromofuran in 20 cc. of anhydrous ether was treated in small portions with 3 g. of magnesium-copper alloy that had been heated gently with 1.5 g. of iodine. The addition of each portion of the alloy was accompanied by a vigorous reaction but a considerable excess of magnesium remained undissolved when the reaction subsided. The ethereal solution of 2-furylmagnesium bromide which resulted was red-brown in color and gave a strong color test for R–MgX with Michler's ketone, by the procedure of Gilman and Schulze.[18]

2-Furoic **Anilide.**—The solution obtained above was decanted from the residual magnesium–copper alloy and an ethereal solution of 1.2 g. of phenyl isocyanate was added dropwise, with constant stirring. A vigorous reaction occurred and after thorough shaking the solution still gave a strong test for R–MgX. It is advisable to avoid an excess of phenyl isocyanate, since the diphenylurea formed upon subsequent hydrolysis is difficultly separated from the anilide. The reaction product was hydrolyzed in the usual way, and the crude 2-furoic anilide was crystallized twice from alcohol, with the addition of decolorizing charcoal, and finally from water; m. p. 121–122° (corr.). For comparison, a sample of 2-furoic anilide was prepared from furoyl chloride and aniline; m. p. 121–122° (corr.). A mixture of the two specimens melted at the same temperature, 121–122° (corr.). The melting point of this compound is reported by previous investigators as 123.5°.[19]

2-Furoic Acid.—A solution of 2-furylmagnesium bromide prepared as above from 5 g. of 2-bromofuran gave a curdy precipitate when treated with carbon dioxide. The reaction mixture was decomposed with dilute sulfuric acid and the ether layer extracted with sodium hydroxide solution. The alkaline extract was acidified and extracted repeatedly with ether. The ether extracts on evaporation left a residue of crystals mixed with a tarry impurity. Sublimation gave crystals of 2-furoic acid, which was identified by comparison with furoic acid obtained from furfural.

Summary

A satisfactory method has been devised for the preparation of the simple halogenated furans from the corresponding halogenated furoic acids. 2-Chloro-, 3-chloro-, 3,4-dichloro-, 2,3,4-trichloro- 2-bromo- and 3-bromofuran have been prepared in a state of purity and their properties described.

The halogen atoms in these compounds were found to be extremely unreactive. No metathetical reactions could be effected with a number of reagents either in aqueous or anhydrous media.

A Grignard reagent, 2-furylmagnesium bromide, was prepared from 2-bromofuran in ethereal solution. This substance reacts normally with carbon dioxide and with phenyl isocyanate to produce 2-furoic acid and 2-furoic anilide.

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[17] Marvel, Blomquist and Vaughn, THIS JOURNAL, 50, 2810 (1928).

[18] Gilman and Schulze, *ibid.*, 47, 2002 (1925).

[19] Schiff, Ann., 239, 367 (1887); Leimbach, J. *prakt. Chem.*, [2] 65, 35 (1902); Baum, *Ber.*, 37, 2954 (1904).

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF WISCONSIN, AND THE OFFICE OF CEREAL CROPS AND DISEASES, BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE ELEMENTARY COMPOSITION OF THE PENTOSAN XYLAN[1,2]

BY KARL PAUL LINK

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Introduction

When it was demonstrated by Wheeler and Tollens[3] that xylose, the sugar which Koch[4] had originally described and isolated from the products of hydrolysis of wood gum, was a pentose sugar with the empirical composition $C_5H_{10}O_5$, it became very probable that the corresponding anhydride, xylan, had the composition $(C_5H_8O_4)_n$. Soon after the relationship of xylan to xylose was established, a controversy arose with respect to the elemental composition of xylan. In 1896 Johnson[6] reviewed the controversy initiated by the conflicting analyses of Thomsen, Koch, Schuppe, Wheeler and Tollens. The analyses reported, with the exception of those by Schuppe, agreed with the formula $(C_5H_{10}O_5)_n$. Schuppe's analyses for the most part gave higher figures for carbon and hydrogen. The analyses reported by Johnson were on a xylan preparation from corn (Zea Mays) cobs. He concluded that xylan has the empirical formula $(C_5H_8O_4)_n$ and that the discrepancies and disagreements reported by other investigators were mainly attributable to the fact that xylan is a very hygroscopic substance, difficult to maintain at a constant moisture content. Although the analyses reported by Johnson appear to have been conducted with the necessary precaution, the conclusion that he reached with respect to the empirical formula of the pentosans was apparently not accepted. The third edition of the late B. Tollens'[6] excellent treatise on the carbohydrates published in 1914 still gave the empirical formula

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[1] Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

[2] The major part of this research was done during 1925–1927 while the author was a Fellow of the International Education Board posted at the University of St. Andrews, Scotland, and the University of Graz, Austria. The author wishes to acknowledge his indebtedness to Sir James Irvine, D.Sc., F.R.S., Principal and Vice Chancellor of the University of St. Andrews, for the privilege of extending the research while a student in his laboratory. The author is particularly indebted to Professor Fritz Pregl, Director of the Medico-chemical Institute of the University of Graz, under whose personal direction the micro-analytical analyses were conducted. To the Board of Directors of the International Education Board, New York City, the author wishes to extend his thanks for the Fellowship grant which enabled him to complete the work in the laboratories mentioned.

[3] Wheeler and Tollens, **Ann.,** 254, **316 (1889).**

[4] Koch, ***Ber.,*** 20, Ref., 145 **(1887).**

[5] Johnson, THIS JOURNAL, **18,214 (1896).**

[6] B. Tollens, "Kurzes Lehrbuch der Kohlenhydrate," Barth, Leipzig, 1914, p. 474.

for xylan as $(C_{10}H_{18}O_9)_n$ or $(C_5H_9O_{4.5})_n$. In fact the old controversy on the question of the elemental constitution of the pentosans still persists at the present time.

The expression $(C_{10}H_{18}O_9)_n$ has again been advanced by Schorsch,[7] who formulates the expression $(C_{10}H_{18}O_9)_n$ for the formula of the pentosans on the evidence that: (1) a quantitative recovery of the corresponding pentose sugar is not attainable; (2) the purest preparations available when distilled with 12% hydrochloric acid by the Kröber–Tollens method never give an amount of furfural estimated as the phloroglucide compound corresponding to more than 92–96% pentosan; **(3)** no sugar other than a pentose has ever been isolated from a pentosan. According to Schorsch the formula $(2C_5H_{10}O_5 \cdot H_2O)_n$ equivalent to $(C_{10}H_{18}O_9)_n$ is in accord with the experimental results. However, it must be borne in mind that it is not possible to hydrolyze pentosans with weak acids without the formation of some decomposition products, and that attempts at a quantitative crystallization of the free pentose sugar are always accompanied by mechanical losses and some retention of sugar in the mother liquors. In addition, it is well known that the Kröber–Tollens method never gives quantitative results even with the free pentoses.

Heuser and Schorsch[8] have advanced evidence that under certain conditions xylan retains sodium hydroxide and appears to form the compound $((C_5H_8O_4)_2 \cdot NaOH)_n$ corresponding to the formula of the hydrate $((C_5H_8O_4)_2 - H_2O)_n$, the formula implicated in the expression $(C_{10}H_{19}O_9)_n$. It should be noted, however, that the union formed with xylan and alkali is an exceedingly labile one, since the sodium hydroxide can readily be eliminated. In addition, it is important to take cognizance of the fact that specimens of anhydrous xylan can be readily obtained by desiccation at 115° in a vacuum of 15 mm., or over phosphorous anhydride at a lower temperature.

In a recent paper from the laboratory of Professor Haworth in Birmingham, England, methylation studies have been extended to the pentose polysaccharides. In this research Haworth and co-workers[9] used a xylan preparation obtained from esparto cellulose. By the method of estimating separately the carbon and hydrogen, and then the moisture content of an air-dried xylan sample, they concluded that their work substantiated the empirical formula $(C_5H_8O_4)_n$. It is apparent that a definite empirical formula for the pentosans is essential for a critical consideration of the molecular constitution of the pentose polysaccharides. In 1926, while the writer was at the laboratory of Professor Fritz Pregl, Graz, Austria, engaged in elementary micro-organic analyses, it was possible to investigate

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[7] Schorsch, *Papier-Fabr. Tech. Wiss., Teil,* 1927, *576–577; C. A.,* 22, *4478* (1928).

[8] Heuser and Schorsch, *Cellulosechemie,* 9, 109 *(1928).*

[9] Hampton, Haworth and Hirst, J. *Chem. Soc.,* 130,1739 (1929).

the problem of the empirical composition of xylan, by micro-combustion methods.

The results obtained from the analyses of 15 xylan specimens from various sources corroborate the contention of Johnson, Haworth and coworkers in formulating xylan as $(C_5H_8O_4)_n$ and the methylated xylan compounds as derivatives of this parent formula.

Experimentation

Five xylan preparations from corn *(Zea Mays)* seedlings isolated as described in this Journal,[10] four xylan specimens from corn cobs, two from corn stalks and one each from beech wood, cherry wood, rye straw, and esparto grass were subjected to the ultimate carbon and hydrogen analysis by the Pregl micro-combustion method.[11] With the exception of the xylan specimens prepared from the corn seedlings, which were isolated as stated above, the various specimens were prepared by the method of Wheeler and Tollens.[12] After the initial isolation the various specimens were subjected to a further purification using the method of Heuser.[13] The preparations were thrice precipitated from 5.0% sodium hydroxide solution (carbonate free) as the copper–xylan complex, from which the copper was eliminated as already described.[14] All of the freshly precipitated preparations were first dried through the use of organic solvents; the importance and significance of this procedure has already been mentioned.[15] When the moisture content of the various xylan preparations was reduced to less than 3% through the employment of the aforementioned technique, no difficulty was encountered in obtaining an absolutely anhydrous xylan by drying the specimens in the Pregl micro-desiccator block at 100° for eight to ten hours at 15 mm. pressure. While it may not be difficult to produce absolutely dry xylan specimens by drying in the Pregl micro-desicca-

TABLE I

ANALYTICAL RESULTS

Source of xylan specimen	Carbon found,[a] %	Hydrogen found,[a] %	Source of xylan specimen	Carbon found,[a] %	Hydrogen found,[a] %
Corn seedlings preparation A	45.23	6 09	Beech wood	45.42	6.08
			Esparto cellulose	45.22	5 85
Corn seedlings preparation B	45.23	6.08	Cherry wood	45.10	5.91
			Rye straw	45.44	6.06
Corn seedlings preparation C	45.22	6.02	Corn cobs 1	45.51	6.09
			Corn cobs 2	45.48	6 10
Corn seedlings preparation D	4524	6.02	Corn cobs 3	45.42	6 04
			Corn cobs 4	45.46	6 04
Corn seedlings preparation E	45.24	6.06	Corn stalks 1	45.47	6.04
			Corn stalks 2	45.47	6.10

[a] All figures are the averages of duplicate analyses of the same specimen.

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[10] Link, THIS JOURNAL, 51, 2506 (1929).

[11] The xylans from beech wood and esparto grass were isolated and purified while the writer was at the St. Andrews Laboratory. All the others had been isolated and purified in the home laboratory.

[12] Wheeler and Tollens, *Ann.*, 254, 304 (1889).

[13] Heuser, *J. prakt. Chem.*, 104, 259 (1922). This method is a modification of the original Salkowski method, *Z. physiol. Chem.*, 34, 162 (1901).

[14] Link, THIS JOURNAL, 51, 2510 (1929).

[15] Link, *ibid.*, 51, 2508 (1929).

tor block, it is necessary to employ the utmost care to prevent a re-absorption of water. This difficulty was circumvented by placing enough of the partially dried xylan specimens in a platinum combustion boat to insure a sample of from six to eight milligrams when completely dry. The boat was then quickly transferred to a micro-weighing bottle by holding the mouth of the bottle against the drying tube and tilting the latter to discharge the boat. After weighing the specimen the boat was expeditiously transferred to the combustion tube in the manner described above. Through the use of this technique the absorption of water from the atmosphere was practically nil, as indicated by control weighings made on samples in platinum boats that were transferred back and forth from the combustion tube to the weighing bottle. The carbon and hydrogen values obtained in the highly purified xylan specimens are given below, calculated on the moisture and ash-free basis. Calcd. for $(C_5H_8O_4)_n$: mol. wt., 132.06; C, 45.44; H, 6.11.

In conclusion the writer wishes to express his gratitude to Dr. Arnulf Soltys (Graz) for the generous assistance and helpful suggestions that he contributed to this work.

Summary

The analytical results obtained by subjecting fifteen highly purified xylan specimens from various sources to the ultimate carbon and hydrogen analyses by the Pregl micro-method, indicate that pure xylan has the empirical formula $(C_5H_8O_4)_n$. This is in agreement with the theoretical formula for xylan when formulated as the anhydride corresponding to xylose, $C_5H_{10}O_5$. Judging from the ultimate analyses of xylan preparations reported in the literature, pure xylan has in most cases either not been obtained, or the preparations were analyzed under conditions that did not exclude the absorption or loss of water in the course of the analytical procedure.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

THE STRUCTURAL ISOMERS OF BROMOBENZOYLACRYLIC ACID

BY GRACE POTTER RICE

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In a recent paper published from this Laboratory[1] two pairs of unsaturated bromo-γ-ketonic esters and the pair of acids corresponding in configuration to them were described and shown to be geometrical isomers, but the position of the bromine atoms in these substances was not determined. In 1925 Bogert and Ritter[2] prepared an unsaturated bromo acid of benzoylacrylic acid and stated that the bromine atom in this substance was probably in the a-position because it gave acetophenone on

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[1] Rice, THIS JOURNAL, 50, 1481 (1928).

[2] Bogert and Ritter, *ibid.*, 47, 526 (1925).

treatment with sodium hydroxide. This bromobenzoylacrylic acid was prepared by the elimination of hydrogen bromide from the two racemic dibromo acids $C_6H_5COCHBrCHBrCOOH$; the position of the bromine atom in the unsaturated acid is, therefore, determined by the comparative reactivities of the two hydrogen atoms in the dibromo acids. Since the mode of addition to benzoylacrylic ester and its substitution products, which have two conjugated systems of double linkages $C_6H_5\overset{1}{O}\overset{2}{C}\overset{3}{C}\underset{4}{H}{=}\overset{4}{C}\underset{3}{H}\underset{2}{C}\underset{1}{O}OR$, has been shown to be a result of 1,4-addition according to the scheme $C_6H_5\overset{1}{O}\overset{2}{C}\overset{3}{C}H{=}\overset{4}{C}HCOOR$,[3,4] it seemed probable that the hydrogen atom α to the C_6H_5CO group would be the reactive one and that the unsaturated acid would, therefore, hold its bromine atom in the β-position to the COOH group. This has been proved to be the case. The proof rests on the synthesis of the structural isomer of the acid of Bogert and Ritter from bromomaleic anhydride by the Friedel and Crafts reaction. This new acid gives phenylglyoxal on ozonization; it is the a-acid, $C_6H_5COCH{=}CBrCOOH$. The acid of Bogert and Ritter must, therefore, be the β-acid $C_6H_5COCBr{=}CHCOOH$.

Since the isomeric unsaturated bromo acids recently described were prepared by elimination of hydrogen bromide from dibromo acids which are substitution products of the dibromobenzoylpropionic acids, they too, undoubtedly, hold their bromine atoms in the β-position. They are, accordingly, $(CH_3O)_2C_6H_2BrCOCBr{=}CHCOOH$ and their esters $(CH_3O)_2C_6H_2BrCOCBr{=}CHCOOR$.

Experimental Part

Before the structure of the bromobenzoylacrylic acids was established, the Friedel and Crafts reaction with bromosuccinic anhydride and benzene was carried out with the idea that if the course of the reaction was such that either a- or β-bromobenzoylpropionic acid was formed exclusively, a clue would be given as to the position of the bromine atom in the bromobenzoylacrylic acid formed in the analogous reaction with bromomaleic anhydride and benzene. The evidence sought was not obtained because not one but two unsaturated bromo acids were isolated from bromomaleic anhydride.

A solution of 14.4 g. of bromosuccinic anhydride in 60 g. of benzene was stirred mechanically and warmed while it was treated gradually with 25 g. of aluminum chloride; the product, which was thrown to the sides of the flask as a solid, was decomposed cautiously with ice and hydrochloric acid and the solution extracted five times with benzene. The benzene deposited 3.7 g. of solid melting at 110–117° which was purified

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[3] Kohler and Engelbrecht, THIS JOURNAL, 41, 764 (1919).

[4] Rice, *ibid.*, 50, 233 (1928).

by boiling it with carbon disulfide and crystallizing the residue from benzene; 2.5 g. of a-bromobenzoylpropionic acid, melting at 118° into a red liquid, was obtained.

Anal. Calcd. for $C_{10}H_9O_3Br$: C, 46.69; H, 3.50. Found: C, 47.09; H, 3.93. It is the acid prepared by Bougault[5] by addition of hydrogen bromide to benzoylacrylic acid. Evaporation of the benzene and carbon disulfide filtrates left a red oil from which boiling water extracted 1.6 g. of benzoylacrylic acid. This was formed from the maleic anhydride which separated during the distillation of bromosuccinic anhydride under diminished pressure. Extraction of the original aqueous solution with ether gave 9 g. of bromosuccinic acid; the yield of a-bromobenzoylpropionic acid calculated from the bromosuccinic anhydride which reacted was 30%. No β-bromobenzoylpropionic acid could be found though seed was available for inoculation. The behavior of bromosuccinic anhydride is thus different from that of methylsuccinic anhydride,[6] which gives both a- and β-substituted ketonic acids in the Friedel and Crafts reaction.

a-Bromobenzoylacrylic Acid, $C_6H_5COCH{=}CBrCOOH$.—The bromomaleic anhydride used for the preparation of this acid by the Friedel and Crafts reaction was made from both isodibromosuccinic acid[7] and from dibromosuccinic acid.[8] From dibromosuccinic acid an 81% yield of the unsaturated anhydride was obtained[9] by heating the acid with half its weight of phosphorus pentoxide at 200–210° until hydrogen bromide was no longer eliminated, distilling the product (b p. 215–216°) and redistilling it under reduced pressure with fresh phosphorus pentoxide—b. p. 110° at 18 mm.

A solution of 24.5 g. of freshly distilled bromomaleic anhydride in 80 g. of benzene was warmed and treated gradually with 38 g. of aluminum chloride with constant stirring. When the vigorous evolution of hydrogen chloride slackened, the product was heated for one hour, the viscous mass treated cautiously with ice and concd. hydrochloric acid and the brownish colored solid filtered off; 18 g. of crude acid melting at 110" into a cherry-red liquid was obtained. The acid was purified by recrystallization from benzene, from which it separates in fine needles; it can also be recrystallized from ether, chloroform, benzene and ligroin, chloroform and ligroin and boiling water. By using water it is possible to get rid of the trace of color which is carried down with other solvents. When impure the acid is extremely sensitive to heat; on evaporation of its solution the residue is a cherry-red oil. From 18 g. of crude product 11.1 g. of pure acid, melting at 129° into a red liquid, was separated.

Anal. Calcd. for $C_{10}H_7O_3Br$: C, 47.05; H, 2.74. Found: C, 47.00; H, 3.01.

The aqueous filtrate, after removal of the crude acid, was extracted four times with benzene; the first crop of crystals from the benzene was 1.5 g. of pure β-bromobenzoylacrylic acid (109°) identified by comparison with a specimen of this acid. The benzene filtrate deposited 2.2 g. of acid, melting at 85–110° into a red oil, from which 1.5 g. of p-bromo acid was separated. This acid gave a colorless melt which solidified on cooling. The residue from benzene as well as the residue left after purifying the a-bromo acid contained a mixture of the a- and β-bromo acids which was contaminated with oily decomposition products. The solid separated from these residues was a mixture of isomeric acids. A trace of the a-bromo acid in the β-bromo acid can invariably be detected because the melt shows the characteristic red color of the a-isomer. The mixture of the a- and β-bromo acids melts at 90–102°. It is an interesting fact that the α-bromo saturated acid and the a-bromo unsaturated acid form red oils on melting, whereas the β-bromo saturated acid and the β-bromo unsaturated acid melt into colorless liquids.

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[5] Bougault, *Ann. chim. phys.*, [8] 15,491 (1908).

[6] Mayer and Stamm, *Ber.*, 56, 1424 (1923).

[7] McKenzie, J. Chem. *Soc.*, 101, 1200 (1912).

[8] Terry and Eichelberger, THIS JOURNAL, 47, 1067 (1925).

[9] Walden, *Ber.*, 30, 2886 (1897).

Ozonization of a-Bromobenzoylacrylic Acid.—Ozonized oxygen containing about 5% of ozone was passed for one and one-half hours through a solution of 1 g. of α-bromobenzoylacrylic acid in 25 cc. of glacial acetic acid at ordinary temperature. The ozone was then swept out with a current of nitrogen, the solution diluted with water. neutralized with sodium carbonate and extracted with ether. The ether was pumped off in the presence of water and the resulting water solution treated with a slightly acid solution of phenylhydrazine. This produced a yellow precipitate which was dried and recrystallized from low-boiling petroleum ether. It separated in the characteristic needles of the low-melting phenylhydrazone of phenylglyoxal, with which it was identified by a mixed melting point.

On boiling with water a-bromobenzoylacrylic acid gives acetophenone, which was identified by its semicarbazone. With warm sodium methylate the acid also gives acetophenone. In one case when steam was passed into the crude product from the Friedel and Crafts reaction in order to remove benzene, acetophenone was formed instantly and not a trace of the unsaturated bromo acids was found after steam distillation had been continued for fifteen minutes. The red oil, which separated from the aqueous layer, solidified in contact with ether into a brick red powder which held no bromine and did not melt below 250°. This behavior of a-bromobenzoylacrylic acid suggests the reactions of benzoylacrylic acid by which von Pechmann[10] prepared a red dye.

Before the structure of a-bromobenzoylacrylic acid was established by ozonization, this acid was treated with sodium hydrosulfite in the hope of reducing it to one of the known saturated bromobenzoylpropionic acids, but the reduction product was benzoylpropionic acid. This reaction is similar to that in which chlorodibenzoylethylene is changed into dibenzoylethane.[11]

Methyl **a-Chlorobenzoylacrylate,** $C_6H_5COCH{=}CClCOOCH_3$.—This unsaturated chloro ester was obtained by saturating a methyl alcohol solution of the a-bromo acid with hydrogen chloride and allowing it to stand. The crude product of reaction was used for analysis.

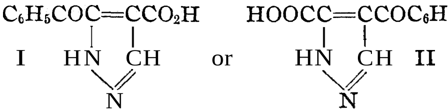
Anal. Calcd. for $C_{11}H_9O_3Cl$: C, 58.79; H, 4.00; Cl, 15.81. Found: C, 58.35; H, 4.17; Cl, 15.76.

The ester remains a yellow liquid after exposure to diffused daylight for a year; it is probably formed by addition of hydrogen chloride followed by elimination of hydrogen bromide.

Methyl a-Bromobenzoylacrylate, $C_6H_5COCH{=}CBrCOOCH_3$.—This ester was prepared by refluxing a methyl alcohol solution of the acid containing a trace of concd. sulfuric acid for three hours. The yellow liquid product is stable in the light but on distillation in a vacuum half of the material was left behind as a red oil; the ester which distilled at 198–200° at 25 mm. was amber colored.

Anal. Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.34. Found: C, 49.64, 49.70; H, 3.77, 3.49.

5-Benzoylpyrazole-4-carboxylic Acid or 4-Benzoylpyrazole-5-carboxylic Acid,



I $C_6H_5COC{=}CCO_2H$ (HN–N=CH ring) or $HOOCC{=}CCOC_6H_5$ (HN–N=CH ring) II .—The reaction between α-bromobenzoylacrylic acid and diazomethane was carried out for the purpose of determining whether the yellow liquid ester corresponds in configuration to the acid. An absolute ether

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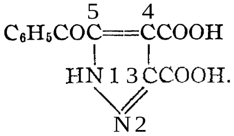
[10] Von Pechmann, Ber., 15, 885 (1882).

[11] Conant and Lutz, THIS JOURNAL, 47, 883 (1925).

solution of diazomethane was added to an absolute ether solution of the acid until evolution of nitrogen ceased; evaporation of the solvent left a yellow oil which gave on analysis a percentage of carbon 3.6% too high for the ester. This yellow oil, after standing for several hours, began to deposit a colorless solid and finally was almost completely changed into this solid. By extracting the mixture with ether the solid was separated from a small quantity of yellow liquid which contained bromine, was insoluble in sodium carbonate solution, was stable in the sunlight, gave acetophenone on warming with water and was probably the ester described above. The solid separated from methyl alcohol in rosets of fine, colorless needles melting at 218° with evolution of gas.

Anal. Calcd. for $C_{11}H_8O_3N_2$: C, 61.11; H, 3.70; N, 12.96. Found: C, 60.76, 61.00; H, 3.71, 4.02; N, 12.86.

The hydrogen bromide is undoubtedly eliminated after formation of the ring nitrogen compound. This reaction is like that of the ester of a-bromocinnamic acid with diazoacetic ester which gives an intermediate product containing bromine.[12] A pyrazole derivative melting at 220" with evolution of gas was made by Wolff,[13] and shown to be



$$\begin{array}{l} \overset{5}{C_6H_5COC}{=\!=}\overset{4}{C}COOH \\ \quad\;\; | \qquad\quad | \\ \quad HN\,1\;\;3\,CCOOH \\ \qquad\;\; \diagdown\!\!\diagup\!\!\diagup \\ \qquad\quad N\,2 \end{array}$$

Since the elimination of carbon dioxide from the COOH at 3 is known to take place more readily than from the COOH at 4, it might be possible to determine the structure of the pyrazole formed from the a-bromo acid by obtaining it or its isomer by removal of carbon dioxide[14,15] from the pyrazole of Wolff. The importance of deciding between the two possible structures for the pyrazole, however, did not seem to warrant the laborious synthesis of Wolff's substance. Since it is known that the carbon of the diazomethane molecule adds to the 8-carbon atom of an unsaturated substance,[16] it is probable that formula I represents the structure of the pyrazole.

In order to prepare the unsaturated bromo acid[2] now proved to be β-bromobenzoylacrylic acid, for purposes of comparing it with the α-bromo acid, it was necessary to brominate benzoylacrylic acid. Von Pechmann,[10] who recrystallized the dibromo acid prepared in chloroform solution from dilute alcohol, gives a melting point of 135° and Bougault,[5] who recrystallized it from carbon disulfide and benzene, gives 148" as its melting point. Bogert and Ritter[Z] report a yield approximately quantitative by bromination of benzoylacrylic acid in glacial acetic acid and give 147.5" as the melting point of the dibromo acid. They state that this is prepared by bromination in chloroform or glacial acetic acid and that search for the second racemic isomer was in vain. In this Laboratory a mixture of racemic isomers was invariably obtained on bromination in both chloroform and glacial acetic acid; this reaction was carried out five times and always a quantitative yield of solid was obtained melting at 110–125°. From this mixture one of the isomers can be separated by boiling the crude solid with benzene and filtering off the less soluble portion, boiling this again with benzene and finally recrystallizing the residue from the same solvent; from 22.6 g. of the mixture 10.1 g. of the dibromo acid which melted at 150° was thus isolated. The rest of the mixture resisted separation though ten different solvents were used. The isomeric dibromo acid can be

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[12] Buchner and Fritsch, Ber., 26,256 (1893).

[13] Wolff, *Ann.*, 325, 187–189 (1902).

[14] Buchner and Dessauer, ***Ber.***, 26, 260 (1893).

[15] Koenigs and Koerner, ***ibid.***, 16, 2153 (1883).

[16] Von Pechmann and Burkard, ***ibid.***, 33,3590,3594 (1901).

separated, however, by starting with the product of bromination melting at 110–125" and boiling it in carbon disulfide, filtering off the less soluble portion, boiling the solid which crystallizes from the carbon disulfide again with this solvent, filtering off the less soluble portion and allowing the filtrate to crystallize. The first crop of crystals from this solution melted at 148°; the mixture of this acid and the solid melting at 150° melted at 110–132°.

This lower-melting isomer, described as a solid melting at 142°, has been prepared from isodibromosuccinic anhydride by the Friedel and Crafts reaction.[2] It readily can be obtained by bromination of benzoylacrylic acid in carbon disulfide solution; 2 g. of the acid was suspended in carbon disulfide and the calculated quantity of bromine added with vigorous stirring. Suddenly the bromine color disappeared and the solution at once deposited 2.8 g. of solid melting at 140–145°; including the residue which was a mixture of isomers, the yield was quantitative. The 2.8 g. of solid was recrystallized twice from chloroform, from which it separates in clusters of needles melting at 148°; 50% of the product was separated as this isomer. It crystallizes from benzene in clusters of fine needles while the isomer (150°) separates in long needles from this solvent. There is no depression in the melting point when the isomer (148°) from bromination in carbon disulfide is mixed with the isomer (148°) described above. A mixture of it and the acid (150°) melts at 110–132°. A mixture of the isomers was recrystallized from benzene; the crystals which separated looked like one substance but they melted at 110–143°.

Isomeric Methyl **Dibromobenzoylpropionates, $C_6H_5COCHBrCHBrCOOCH_3$.**—An absolute ether solution of the isomer (150") was treated with an absolute ether solution of diazomethane; evaporation of the solvent left a colorless solid in quantitative yield which melted at 58° after one recrystallization from methyl alcohol.

Anal. Calcd. for $C_{11}H_{10}O_3Br_2$: C, 37.71; H, 2.85. Found: C, 37.83; H, 3.08.

When the isomer (148") was likewise treated with diazomethane and the solid recrystallized from methyl alcohol, a quantitative yield of ester melting at 48° was obtained.

Anal. Calcd. for $C_{11}H_{10}O_3Br_2$: C, 37.71; H, 2.85. Found: C, 37.80, 37.70; H, 3.08, 3.11.

The mixture of the two esters is a liquid. These esters were prepared in order to confirm a statement made in an earlier paper[17] that bromination of methyl benzoylacrylate gives a product which fails to crystallize because it is a mixture of racemic isomers. The liquid product of bromination of this ester was seeded with the dibromo ester (58°); after standing for several days a crop of crystals which were the ester (58°) separated.

When β-bromobenzoylacrylic acid was prepared from dibromobenzoylpropionic acids,[2] 18% of the dibromo acids was recovered unchanged; it is necessary to heat a glacial acetic acid solution of the dibromo acids in a boiling water-bath for one hour with potassium acetate in order to complete the elimination of hydrogen bromide; the highest yield of unsaturated acid obtained in this work was 55%. β-Bromobenzoylacrylic acid separates from benzene in large, transparent crystals melting at 95–98'; on standing these crystals become opaque and give up their solvent gradually. . If the solid (95–98°) is boiled with carbon disulfide, it loses its benzene and shows the melting point reported, 109'.

β-Bromobenzoylacrylic acid does not give a trace of acetophenone on boiling for one hour with water but on heating it for two hours on a boiling water-bath with a 20% sodium carbonate solution, oxalic acid and acetophenone (identified by its semicarba-

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[17] Rice, THIS JOURNAL, 45, 227 (1923).

zone) were formed. With potassium hydroxide solution (15g. in 25 cc. of water) the acid gives acetophenone even when the solution is kept cold with ice; after warming this solution for two minutes a 94% yield of benzoic acid was separated. The behavior of the ***a-*** and β-bromo acids on hydrolysis shows that treatment with alkaline reagents and even boiling with water can offer no clue as to the position of the bromine atom in the unsaturated bromo acids. That an acetylenic compound was formed[2] from dibromobenzoylpropionic acid in the presence of 3 M sodium hydroxide seems improbable in view of the ease of hydrolysis of the unsaturated p-bromo acid which would be the intermediate product formed on treatment with alkali. Further, the tendency which acetylenic compounds of the type $C_6H_5COC{\equiv}CCOC_6H_5$ show to form addition products in the presence of alkaline reagents[1,11] indicates that an acetylenic compound, if formed, would probably not escape reaction. Attempts have been made to prepare benzoylpropiolic acid but it has not yet been obtained in reactions analogous to those used by Lutz[18] for the preparation of dibenzoylacetylene from dibromodibenzoylethane. Further work on this reaction is in progress.

β-Bromobenzoylacrylic acid, like the a-bromo acid, gives benzoylpropionic acid on treatment with sodium hydrosulfite, so that again no conclusion as to structure can be drawn from the reduction reaction.

Methyl **β-Bromobenzoylacrylate,** $C_6H_5COCBr{=}CHCOOCH_3$.—A liquid mixture of isomers was obtained by bromination of 8.3 g. of methyl benzoylacrylate in carbon disulfide solution; this was dissolved in methyl alcohol, the solution heated for five minutes with 8 g. of potassium acetate and poured onto ice. The yellow liquid, obtained by extraction with ether, gave 10.5 g. of product distilling at 180–185° at 20 mm., a 90% yield. On standing, the yellow liquid deposited a colorless solid which melted at 86° after two recrystallizations from methyl alcohol. In the sunlight the yellow liquid is rapidly and completely transformed into the colorless solid. These esters, therefore, are geometrical isomers.

Anal. Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.34. Found: I (86°) C, 49.24; H, 3.54. II (yellow liquid) C, 49.41; H, 3.63.

On treatment of β-bromobenzoylacrylic acid with diazomethane a quantitative yield of the ester (86") was obtained. This ester, then, corresponds in configuration to the known β-bromo acid (109°). These esters are not reduced even on warming with sodium hydrosulfite.

When the β-bromo esters are boiled with water the vapor at first carries a sharp, tear-producing substance which soon disappears and, after several hours of boiling, acetophenone is formed. On slight warming with potassium hydroxide solution both esters give acetophenone and benzoic acid.

In marked contrast to the behavior of a-bromobenzoylacrylic acid, the β-bromo acid gave a bromo ester when its methyl alcohol solution was saturated with hydrogen chloride. This ester (86°) on standing for two days in methyl alcohol saturated with hydrogen chloride was partially changed into a chloro ester. Micro Pregl determinations gave 20.85, 21.59% of halogen; calcd. for Br, 29.73; for Cl, 15.81.

Summary

a-Bromobenzoylacrylic acid has been prepared and its structure proved. A comparison of its reactions and those of the known bromobenzoylacrylic acid, now shown to be a β-substituted acid, has been made.

NEW YORK CITY

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[18] Lutz, THIS JOURNAL, **48,** 2914 (1926).

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXVII. SYNTHESIS OF A NEW DISACCHARIDE KETOSE (LACTULOSE) FROM LACTOSE[1]

BY EDNA M. MONTGOMERY AND C. S. HUDSON

RECEIVED FEBRUARY 3, 1930 PUBLISHED MAY 8, 1930

The comparison of the rotation of sorbose with that of methylsorboside,[2] which indicated that sorbose may possibly exist in solution in only one form, namely, as a-sorbose, opened a line of thought which has led us to undertake the preparation of new ketoses and ketose derivatives. If the fact that several of the known ketose sugars (sorbose, tagatose, mannoketoheptose and α-glucoheptulose)[3] do not show mutarotation is to be ascribed to the existence of these sugars in only one form in solution, one must inquire why these ketoses are unable to undergo the tautomeric balanced reactions which cause the mutarotation of aldoses. In sharp contrast to the behavior of these four ketoses stands the observation that fructose, turanose[4] (which is glucosido-fructose) and perseulose (which is very similar in configuration to fructose)[5] exhibit mutarotation. If the four non-mutarotating ketoses do not change partially in solution from alpha to beta forms of like ring structure, is the mutarotation of the other three due to such a change or may it not rather involve a shifting of the oxygen ring? The fact that fructose mutarotates but its tetra-acetate does not, whereas both glucose and glucose tetra-acetate mutarotate, is indeed evidence that the mutarotation of fructose is caused by ring-shifting; its tetra-acetate cannot shift the ring except by an improbable acetyl migration. With these questions and ideas in mind we have begun the collection of further experimental data on ketoses and their derivatives.

Few ketoses are known in comparison with the large number of aldoses that are recognized. The number may be increased either by the discovery of new naturally occurring ketoses or by way of laboratory synthesis. The discovery of mannoketoheptose in the avocado[5] and of sedoheptose in the stonecrop[6] indicates that a systematic search for other new ketoses in natural products might be well repaid, but for the present the

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[1] Publication authorized by the Director of the Bureau of Standards. Article XXVI was published in THIS JOURNAL, 52,1707 (1930). The synthesis of lactulose was reported by the authors at the April, 1929, meeting of the National Academy of Sciences [*Science,* 69, 556 (1929)]. The name lactoketose was then used for the sugar but it has been decided subsequently to name it lactulose.

[2] Hudson, THIS JOURNAL, 47,278 (1925).

[3] Bertrand and Nitzberg, *Compt. rend.*, 186,925 (1928).

[4] Hudson and Pacsu, *Science,* 69,278 (1929).

[5] La Forge, *J. Biol. Chem.*, 28, 511 (1917).

[6] La Forge and Hudson, *ibid.*, **30,** 61 (1917).

path of synthesis appears to offer prospect of larger or at least more rapid returns.

The conversion of aldoses to ketoses is a rich and only slightly explored field. The first synthesis of this kind was performed by Emil Fischer[7] in the following two ways: (1) glucose → glucose osazone → isoglucosamine → fructose; *(2)* glucose → glucose osazone → glucosone → fructose. Although Fischer was hopeful that these reactions would prove of general application, such has not been the case and no other ketose has been synthesized by them. Philippe's[8] attempt to prepare a ketose from a-glucoheptose through Fischer's methods was unsuccessful. New methods of ketose synthesis, introduced by Bertrand and by Lobry de Bruyn, have led to the discovery of perseulose,[9] α-glucoheptulose,[3] tagatose and *d*-sorbose,[10] the antipode of natural *l*-sorbose. Bertrand has utilized the sorbose bacterium to oxidize alcohols of the sugar group to ketoses but the application of this biological method seems to be considerably restricted by the specificity of the bacterium. The Lobry de Bruyn rearrangement of aldoses and ketoses in alkaline solution appears at the present time to offer the best prospect for synthesizing new ketoses from the large number of known aldoses. The researches of Lobry de Bruyn, Van Ekenstein, and Nef[11] have shown that the important factors for the success of the synthesis are (1) the obtaining of conditions of alkaline concentration, time and temperature which give suitable rearrangement of the aldose with a minimum of side reactions and (2) a separation of the ketose from the mixture of sugars and decomposition products which results from the alkaline treatment of an aldose. The success which Wolfrom and Lewis[12] have reported in the rearrangement of tetramethylglucose and tetramethylmannose at 35° in saturated limewater has led us to select these conditions for the initial step in ketose synthesis. In carrying out the second step the procedure of Nef[11] in a modified form has been used and aldoses have been removed from ketoses by oxidizing them with bromine water under the mild conditions of acidity that result from the presence of a buffering salt such as barium benzoate, as recommended lately by Hudson and Isbell.[13] By applying these reactions to lactose it has been possible to transform it to a new crystalline disaccharide ketose, to which the name lactulose is given because of its origin, and in the following article there is described by our colleague, W. C. Austin, the preparation in similar manner of a new crystalline ketose from d-a-glucoheptose, to which he has given the name *d*-

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[7] Fischer, Ber., **22,** 87 (1889); Fischer and Tafel, ibid., 20, 2566 (1887).

[8] Philippe, *Ann. chim. phys.*, 26,289 (1912).

[9] Bertrand, *Compt.* rend., 147,201 (1908).

[10] Lobry de Bruyn and Van Ekenstein, *Rec. trav. chim.*, 16,262 (1897); **19,** 1 (1900).

[11] Nef, *Ann.*, 403,204 (1914).

[12] Wolfrom and Lewis, THIS JOURNAL, 50,837 (1928).

[13] Hudson and Isbell, ibid., 51,2225 (1929).

glucoheptulose. These results indicate that the directions which we have worked out are probably of general applicability for synthesizing many new ketoses from the large number of aldoses that are known. Work in this field is being continued by the authors and at present the synthesis of d-mannoketoheptose is being attempted.

Behavior of Lactose in Weak Calcium Hydroxide Solution.—A solution of **180** g. of a-lactose monohydrate in one liter of clear limewater of **0.043** normality, which had been prepared by saturating distilled water with slaked lime at 35°, was kept at 35° until the change of rotation that results from the Lobry de Bruyn rearrangement was complete. The initial mutarotation of lactose in such an alkaline solution is very rapid and the first reading, which was made after the lapse of four minutes, showed the equilibrium rotation of lactose, $[\alpha]_D$ +52.5. The rearrangement became noticeable at the end of half an hour, when the rotation was **+50.7.** After twenty-four hours it was +37.7, after thirty-six hours +31.6 and after forty-eight hours +31.5. The time required for the equilibration of lactose, thirty-six hours, is much shorter than that observed by Wolfrom and Lewis for d-glucose under like conditions, which was ten days. The addition of more lime to samples of the equilibrated lactose solution caused no further change of rotation. When the equilibrated solution was analyzed for aldoses by alkaline hypoiodite, using the directions of Goebel,[14] a high result indicating the absorption of more iodine than could be accounted for by all the lactose originally present, was obtained. This result conforms with the observation of Wolfrom and Lewis in the case of the glucose rearrangement and is presumably due, as they have suggested, to the presence of an unsaturated enolic derivative of the aldose. The equilibrated lactose solution was acidified at 10° with sulfuric acid to a normality of **2.0** and kept at 35° for two hours, as recommended by Wolfrom and Lewis, to accomplish de-enolization. Its analysis then by iodine oxidation indicated a mixture of approximately 70% aldose and 30% ketose. Experience in preparing the crystalline ketose from a considerable number of equilibrated solutions indicates that the yield is somewhat increased by the introduction of the step of de-enolization but that the increase is hardly worth the extra labor involved.

Isolation of a New Ketose from the Equilibrated Solution.—If one employs a de-enolized solution, the sulfuric acid is neutralized with calcium carbonate without heating and the filtrate and washings are concentrated under reduced pressure to a sirup. When de-enolization is omitted, the equilibrated solution is reduced similarly to a sirup. In either case the sirup resulting from the treatment of **180** g. of lactose is dissolved in **500** cc. of **95%** alcohol. Lactose crystallizes abundantly (about **110–125** g.) and is filtered off after several days' standing at low temperature. The mother liquor and alcoholic washings are concentrated to a sirup which is then mixed with six volumes of 95% alcohol and the precipitated calcium salts are removed. The filtrate is concentrated again, the sirup obtained is dissolved in **50** cc. of absolute methyl alcohol and allowed to crystallize slowly in a desiccator, yielding a second crop of lactose; repetition of this treatment usually gives a third small crop of lactose, bringing the total recovery to about **120–135** g. Another repetition yields by a slow crystallization, which is much aided by seeding with crystals of lactulose, a crop of about 14 g. of impure ketose of $[\alpha]_D$ **−32** (final) when a de-enolized solution has been employed, or about **11** g. showing $[\alpha]_D$ **−23,** when de-enolization has been omitted. The impure sugar is a mixture of lactulose and presumably lactose; the pure ketose can be obtained from it through the process of oxidizing the aldose with bromine water in the presence of a buffering salt. The amount of aldose present, calculated as lactose, is first estimated

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[14] Goebel, *J. Biol.* Chem., **72, 801** (1928).

by hypoiodite; it is usually about 15% of the total dry matter. Bromine to the extent of 1.1 moles (Br_2) for each mole of aldose present is added to a 10% aqueous solution of the impure ketose containing an excess of barium benzoate (1.25 mole) and the solution is kept at room temperature in the dark for two days. The excess bromine, the barium and the benzoic acid are then removed as described by Hudson and Isbell and the aldobionic acid is converted to a salt (calcium, barium or lead) without heating. The solution is concentrated to a sirup and the salts are precipitated by adding 6 volumes of 95% alcohol, filtering, reconcentrating the filtrate, dissolving it in 250 cc. of absolute alcohol, refiltering and reconcentrating. A solution of the last sirup in an equal volume of absolute methyl alcohol yields by a slow crystallization (seven days) about 65% of the ketose that was present in the impure product; its $[\alpha]_D^{22}$ value is −51.5 (final) and the rotation is not changed by recrystallization from 50% methyl alcohol. The yield of pure lactulose is about 6 to 7.5 g. from 180 g. of lactose or 10 to 15% of the lactose that underwent rearrangement. We have not investigated the other products that are apparently formed in considerable quantity. While the yield of lactulose leaves much to be desired, it is probable that the general application of the method will show better results with many other aldoses because lactulose is very difficult to crystallize; in support of this expectation it is mentioned that Austin (see next article) has obtained much higher yields of *d*-glucoheptulose from d-a-glucoheptose by the method.

Properties of **Lactulose.**—Lactulose crystallizes in hexagonal, colorless plates often grouped in clusters. It melts at 158°, gives the Seliwanoff test for ketoses, is not oxidized by hypoiodite, reduces Fehling's solution on heating and is sweeter than lactose but not as sweet as sucrose. It is an anhydrous sugar of the formula $C_{12}H_{22}O_{11}$. Its combustion shows C, 41.90% and H, 6.50%, whereas the calculated values from this formula are C, 42.09% and H, 6.43%; the freezing-point method indicates its mol. wt. to be 340–352, agreeing with the formula. It is very soluble in water. Lactulose exhibits rapid mutarotation. In aqueous solution at 22° its $[\alpha]_D$ value is −23.8 two minutes after solution and the final value is −51.5. The course of the mutarotation is shown in the table. It follows the unimolecular order and the extrapolated initial rotation is about $[\alpha]_D^{22}$ −5. Since the change is toward the negative and the mutarotating component (fructose, see later) is a d-sugar, the crystalline form of the disaccharide is to be designated a-lactulose. The rate of its mutarotation (0.114) at 22° is approximately the same as that of fructose[15] (0.082 at 20").

TABLE I

MUTAROTATION OF ALPHA LACTULOSE AT 22° IN DILUTE AQUEOUS SOLUTION

Time, minutes	$[\alpha]_D^{22}$	$(k_1 + k_2) = \frac{1}{t} \log \frac{r_0 - r_\infty}{r - r_\infty}$
0	[− 51	..
2	−23.8	0.112
2.6	−27.9	.113
3.6	−32.7	.109
4.3	−36.9	.117
5.7	−41.6	.118
7.1	−44.5	.116
8.7	−46.7	.113
24 hours	−51.5 (constant)	..

Preparation of **Lactone Osazone** and its Anhydride from **Lactulose.**—The phenylosazone of lactulose was not distinguishable from lactose osazone and it showed the unique characteristic of the latter in changing to a crystalline anhydride on heating its

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[15] Hudson and Yanovsky, THIS JOURNAL, 39, 1013 (1917).

solution in dilute sulfuric acid.[16] This anhydride is particularly suitable for the characterization of lactose osazone because it shows a definite rotatory power and does not exhibit mutarotation. We find that lactose osazone, which exhibits mutarotation, shows varying final values and by successive recrystallizations it was not possible to obtain a substance of constant final rotation. The anhydro-osazone from lactose melted at 226° (uncorr.) with decomposition and showed $[\alpha]_D^{20}$ —174 in a mixture of four parts of pyridine and six parts of alcohol[17] (concentration, 2 g. of anhydro-osazone/100 cc.). The anhydro-osazone from lactulose melted at 226 with decomposition and showed $[\alpha]_D^{20}$ −174. A mixture of the two products melted at 225–226 with decomposition. The nitrogen content of the anhydro-osazone from lactulose by the Dumas method was 11.06%; theory requires 11.15%. Finally, the identity of the anhydro-osazones from the two sugars was conclusively established by solubility measurements of the two substances in acetone at 5°. The solubility of the anhydro-osazone from lactose was 0.1484 g./100 cc. from supersaturation and 0.1476 from undersaturation, and the corresponding values for the anhydro-osazone from lactulose were 0.1492 and 0.1480. The possibility that the anhydro-osazones might be different compounds of closely agreeing solubilities and other properties was tested by a measurement of the solubility of a mixture of equal quantities of the two anhydro-osazones, which gave the values 0.1484 and 0.1492 from under- and supersaturation; these data make it certain that the two products are the same chemical substance because if such were not the case the solubility of the mixture would be the sum of the individual solubilities, approximately 0.297 g. This method of testing the identity of pure substances is somewhat like the method of "mixed melting points" and may well be designated a "mixed solubility" method. It is very sensitive and is recommended in cases where the mixed melting-point method is of questionable significance because of decomposition of the substance.

Identification of the Component Hexoses of **Lactulose.**—A solution of 6 g. of lactulose in 120 cc. of 1% sulfuric acid was kept at 100" for eight hours to accomplish hydrolysis. Exact removal of the acid with barium hydroxide and concentration of the solution under reduced pressure to a thick sirup, which was taken up in very little methyl alcohol, yielded 1.5 g. of a crystalline sugar. After one recrystallization from this solvent, 1.0 g. of the sugar, dried at 50° for six hours, was obtained, showing $[\alpha]_D^{20}$ +81 (final) in aqueous solution; this value agrees with the known rotation of d-galactose. Fructose was isolated from the mother liquor in the form of its crystalline compound with calcium hydroxide, which was then decomposed with the exact equivalent of oxalic acid. Evaporation of the filtrate to a sirup, solution of this in alcohol and slow evaporation in a desiccator yielded 0.36 *g*. of crystalline sugar, of $[\alpha]_D^{20}$ —91.5 (final), which agrees with the known rotation of d-fructose.

The Structure of **Lactulose.**—Lactulose shows the composition and molecular weight of a disaccharide, $C_{12}H_{22}O_{11}$, as has been mentioned. Its reduction of Fehling's solution, the positive Seliwanoff test and the fact that it is not oxidized by bromine or by hypoiodite show that its molecule contains a ketose with a free reducing group. The fact that its anhydro-osazone is identical with lactose anhydro-osazonc shows that its structure is to be expressed as d-galactosido-4-d-fructose, because lactose is known to be d-galactosido-4-d-glucose~and lactose anhydro-osazone can result from no ketose of any other structure. Since lactulose crystallizes as an alpha form, as shown by the direction of its mutarotation, and since lactose is a beta galactosido disaccharide as shown from its hydrolysis by emulsin and from its rotation (see article XXVI[19] of this

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[16] Fischer, **Ber., 20,** 821 (1887).

[17] Neuberg, ibid., **32,** 3386 (1899).

[18] Zemplén, ibid., **60,** 1309 (1927).

[19] Hudson, THIS JOURNAL, 52, 1707 (1930).

series), its structure may be further specified by the designation alpha 4-*β*-*d*-galactosido (1,4)-*α*-*d*-fructose, the 1,4-ring being assigned to the galactose portion because of the ring structure of lactose shown in article XXVI. The ring of the fructose component remains unknown, but it obviously cannot be of the 2,4-type. The isolation of *d*-galactose and d-fructose by the acid hydrolysis of lactulose agrees with the assigned composition.

Summary

As an experimental introduction to the extension of the Lobry de Bruyn rearrangement for the synthesis of new ketoses, conditions for the conversion of lactose to a disaccharide ketose have been studied and a new ketose named lactulose has been isolated in pure crystalline condition. Lactulose is shown to be 4-*β*-*d*-galactosido(1,4)-*d*-fructose and the crystalline sugar is an alpha form.

WASHINGTON, D. C.

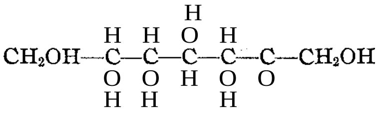
[CONTRIBUTION FROM THE POLARIMETRY SECTION, U. S. BUREAU OF STANDARDS]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXVIII. THE CONVERSION OF d-ALPHA-GLUCOHEPTOSE TO A NEW KETOSE, d-GLUCOHEPTULOSE[1]

BY W. C. AUSTIN

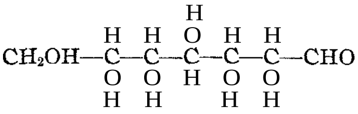
RECEIVED FEBRUARY 3, 1930 PUBLISHED MAY 8, 1930

It is to be expected on structural grounds that a new ketose of configuration **(A)** may be prepared in some suitable way from the known *d*-*α*-glucoheptose, of configuration[2] (B). The osazone of this hypothetical



$$\begin{array}{ccccccccccc} & & & & & H & & & & & \\ & H & & H & & O & & H & & & \\ CH_2OH- & C & - & C & - & C & - & C & - & C & -CH_2OH \\ & O & & O & & H & & O & & O & \\ & H & & H & & & & H & & & \end{array}$$

A



$$\begin{array}{ccccccccccc} & & & & & H & & & & & \\ & H & & H & & O & & H & & H & \\ CH_2OH- & C & - & C & - & C & - & C & - & C & -CHO \\ & O & & O & & H & & O & & O & \\ & H & & H & & & & H & & H & \end{array}$$

B

ketose should be identical with d-glucoheptose osazone, which has been prepared by Fischer[2] through the action of phenylhydrazine on either d-a-glucoheptose or *d*-*β*-glucoheptose. This ketose, to which the name d-*glucoheptulose* might well be given, should bear the same configurational relationship to the epimeric aldoses, d-a- and *d*-*β*-glucoheptose, as does *d*-fructose to d-glucose and d-mannose. The properties of d-glucoheptulose should apparently be of considerable interest because all the asymmetric

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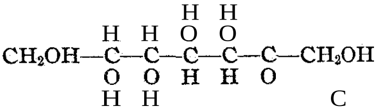
[1] Publication approved by the Director of the U. S. Bureau of Standards. The author was a National Research Fellow in Medicine, 1927–1928. He has arranged with Dr. C. S. Hudson, under whose direction the research was carried out, that it will be included as No. XXVIII in the series entitled "Relations between Rotatory Power and Structure in the Sugar Group." No. XXVII was published in THIS JOURNAL, 52,2101 (1930).

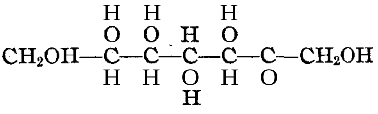
[2] Fischer, ***Ann.,*** 270, 64 (1892).

carbon atoms (Nos. **3,** 4, 5 and 6) of the sugar have precisely the configurations of the corresponding asymmetric carbon atoms (Nos. 2, 3, 4 and 5) of the d-glucose molecule. Also, since d-mannoketoheptose, of configuration[3] C shows no mutarotation, it may be expected that its epimeric[4] ketose,



$$\mathrm{CH_2OH{-}\underset{\substack{O\\H}}{\overset{H}{C}}{-}\underset{\substack{O\\H}}{\overset{H}{C}}{-}\underset{H}{\overset{\substack{H\\O}}{C}}{-}\underset{H}{\overset{\substack{H\\O}}{C}}{-}\underset{\substack{O\\C}}{C}{-}CH_2OH}$$

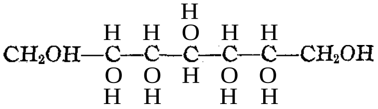
d-glucoheptulose, will not mutarotate. The value of the specific rotation of d-glucoheptulose may indeed be calculated in first approximation by adding the "epimeric difference of molecular rotation" (6700)[5] to the molecular rotation of d-mannoketoheptose ($[\alpha]_D + 29.2$) and dividing by the mol. wt. (210) of glucoheptulose, with the result that $[\alpha]_D = ((29.2)(210) + 6700)/210 = +61$. From these arguments it obviously follows that the antipodal sugar, *l*-glucoheptulose, of configuration



$$\mathrm{CH_2OH{-}\underset{H}{\overset{\substack{H\\O}}{C}}{-}\underset{H}{\overset{\substack{H\\O}}{C}}{-}\underset{\substack{O\\H}}{\overset{H}{C}}{-}\underset{H}{\overset{\substack{H\\O}}{C}}{-}\underset{O}{C}{-}CH_2OH}$$

may be expected to show $[\alpha]_D$ —61, approximately, with no mutarotation.

These deductions from structural theory and rotatory relations appear to have an important bearing upon the results of some recent synthetic work in the sugar group. Bertrand and Nitzberg[6] have obtained a pure crystalline ketose, to which they give the name a-glucoheptulose, by the action of the sorbose bacterium upon a solution containing a-glucoheptitol, of configuration



$$\mathrm{CH_2OH{-}\underset{\substack{O\\H}}{\overset{H}{C}}{-}\underset{\substack{O\\H}}{\overset{H}{C}}{-}\underset{H}{\overset{\substack{H\\O}}{C}}{-}\underset{\substack{O\\H}}{\overset{H}{C}}{-}\underset{\substack{O\\H}}{\overset{H}{C}}{-}CH_2OH}$$

Since Bertrand has shown during his extended researches with this bacterium that the ketose which it produces in a given case results from the oxidation of the secondary alcohol group on the carbon atom that is adjacent to a terminal primary alcoholic carbon atom, he and Nitzberg consider that the bacterium probably oxidizes a-glucoheptitol either at its Carbon 2 or 6 and that the configuration of a-glucoheptulose is thus probably either

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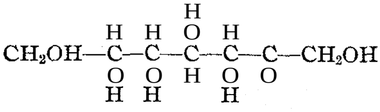
[3] La Forge, *J. Biol. Chem.*, 28, 511 (1917).

[4] The concept of "epimeric" has been developed for aldoses (Votoček) but it is apparent that it can be extended to ketoses; see Hudson, THIS JOURNAL, 52, 1680 (1930). Epimeric aldoses (e. g., d-glucose and d-mannose) differ only in the configuration of their carbon atom 2; epimeric 2-ketoses (e. g., d-glucoheptulose and d-mannoketoheptose) differ only in the configuration of their carbon atom **3.**

[5] Hudson, *ibid.*, 48, 1434 (1926).

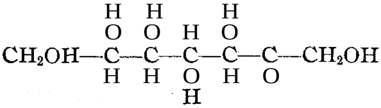
[6] Bertrand and Nitzberg, *Compt.* rend., 186, 925, 1172, 1774 (1928).



$$\mathrm{CH_2OH{-}\underset{OH}{\overset{H}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\underset{H}{\overset{OH}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\underset{O}{C}{-}CH_2OH}$$

d-Glucoheptulose

or



$$\mathrm{CH_2OH{-}\underset{H}{\overset{OH}{C}}{-}\underset{H}{\overset{OH}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\underset{H}{\overset{OH}{C}}{-}\underset{O}{C}{-}CH_2OH}$$

l-Glucoheptulose

These configurations represent antipodal forms of one sugar and the designations d and *l* are used in the sense of the dextro and levo series of Fischer, without regard to the actual directions of rotations of the two enantiomorph~. The researches of Bertrand and Nitzberg have not as yet given a decision between these configurations for their a-glucoheptulose and they use this designation of the ketose in the purely empiric sense that the sugar is derived from a-glucoheptitol. Bertrand and Nitzberg report that α-glucoheptulose shows no mutarotation and that it is levorotatory, $[\alpha]_D$ -67.1. From the agreement of these data with the present deductions from rotatory relations, it seems highly probable that their ketose is *l*-glucoheptulose.

The rotation which has been calculated for d-glucoheptulose (+61) is of interest also in another respect, since it has now become probable from the data of the preceding paragraph that these calculations are substantially correct. The known alpha form of d-mannose (mol. wt. 180) shows[7] $[\alpha]_D$ +30 and the 1,A = 1,4-ring has been assigned to it by Hudson? By use of the epimeric difference of rotation Hudson[S] calculated from this value the rotation of the epimeric alpha d-glucose, of 1,A = 1,4-ring structure, to be $[\alpha]_D = ((30)(180) + 6700)/180 = +67$. Neither of the two known crystalline forms of d-glucose (of $[\alpha]_D$ +113 and +19, respectively), can be this substance and Hudson concluded that the calculated value must refer to a form of d-glucose which has not yet been isolated. If it should now prove possible to isolate a crystalline form of d-glucoheptulose having an $[\alpha]_D$ value of approximately +61, strong evidence would be at hand for the belief that alpha d-glucose of 1,A = 1,4-ring structure rotates near +67, because the calculated rotation of d-glucoheptulose is obtained from that of d-mannoketoheptose by the same method that the rotation of α-*d*-glucose (1,A = 1,4) is obtained from that of a-d-mannose (1,A = 1,4). Moreover, the close agreement between the values of $[\alpha]_D$ for a-d-mannose (1,A = 1,4) (+30) and d-mannoketoheptose (+29.2) has its counterpart in the agreeing calculated rotations of α-*d*-glucose (1,A = 1,4) (+67) and d-glucoheptulose (+61), which may be correlated with the like configurations of the asymmetric carbon atoms in the members of each of these pairs, as has been indicated.

These various considerations and correlations, which were disclosed to me by Dr. Hudson shortly after the appearance of Bertrand and Nitzberg's

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[7] Levene, J. *Biol. Chem.*, 57,329 (1923).

[8] Hudson, THIS JOURNAL, 48, 1424 (1926); 52, 1680 (1930).

[9] Hudson, abid., 48, 1434 (1926).

first paper, made the synthesis of d-glucoheptulose from d-a-glucoheptose by some chemical method which would leave no uncertainty regarding the configuration of the resulting ketose appear very desirable and the work was accordingly undertaken. It was noticed that Philippe[10] had sought to accomplish this synthesis through the reactions d-a-glucoheptose ⟶ *d*-α-glucoheptose osazone ⟶ d-glucoheptulose, which would be analogous to the methods by which Fischer[11] converted d-glucose to d-fructose, but that he was unable to carry out the second stage. Repetition of Philippe's work by the writer led likewise to failure. Success came, however, through the use of Lobry de Bruyn's method of conversion of an aldose to a ketose in weakly alkaline solution. It has been possible in this way to synthesize d-glucoheptulose with a yield of about 30% by applying to *d*-α-glucoheptose the procedure through which Montgomery and Hudson[12] have recently synthesized lactulose from lactose in this Laboratory. Proof that the new heptose is a ketose was readily obtained from the observation that it is not oxidized by bromine water. Since its osazone proved to be identical with that of d-a-glucoheptose in analysis, melting point and mixed melting point, solubility and mixed solubility,[12] rotation and mutarotation, it seems certain that the ketose has the indicated configuration of *d*-glucoheptulose. The sugar crystallizes in prisms of m. p. 171–174°, shows no mutarotation and is dextrorotatory, $[\alpha]_D^{20}$ +67 in dilute aqueous solution. These results, which have been very carefully established, agree in every respect with the theoretical deductions from rotatory relations. They show that the a-glucoheptulose of Bertrand and Nitzberg is *l*-glucoheptulose (m. p. 173.5°, $[\alpha]_D$ -67), the optical antipode of the synthetic *d*-glucoheptulose. The existence of this d-glucoheptulose, of $[\alpha]_D$ $+67$, is strong experimental evidence that Hudson's calculation of 4-67 for the rotation of the now unknown a-d-glucose, of the 1,A = 1,4-ring structure, is substantially correct.

Preparation of *d*-Glucoheptulose.—Following the directions of Wolfrom and Lewis[13] for the enolization of aldoses in alkaline solution, a saturated solution of calcium hydroxide in water at 35° was prepared and some d-a-glucoheptose was dissolved in it to make a 10% solution. At 35° the $[\alpha]_D$ value changed from an initial rotation of about $-$**20,** the equilibrium rotation of d-a-glucoheptose, to $-$**17** after one hour, 0 after ten hours, +**30** after forty-six hours, and became constant after about seven days at +**40.** An iodine estimation of aldoses in this equilibrated solution showed about 40% aldose and 60% ketose. In a second experiment the end rotation was $[\alpha]_D$ +35. These two solutions, representing **55** g. of d-a-glucoheptose, were united and concentrated under reduced pressure to about **75** cc. and an equal volume of methyl alcohol was mixed with the sirup. A crop of **4.5** g. of crystalline d-a-glucoheptose separated from the solution when it was kept overnight in the ice box. A second crop of 5 g. of the original aldose

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[10] Philippe, *Ann. chim. phys.*, **26,324 (1912).**

[11] Fischer, ***Ber.*, 22, 87 (1889);** Fischer and Tafel, ***ibid.*, 20,2566 (1887).**

[12] Montgomery and Hudson, THIS JOURNAL, **52,2101 (1930).**

[13] Wolfrom and Lewis, *ibid.*, **50, 837 (1928).**

was obtained from the mother liquor by concentration and like treatment. The second mother liquor was concentrated to a thick sirup which was dissolved in about 600 cc. of methyl alcohol. An amorphous residue was filtered off, 200 cc. of absolute ether was added to the filtrate and more amorphous material was filtered off with the aid of decolorizing carbon. The clear and nearly colorless filtrate was concentrated to a sirup, taken up in about 45 cc. of alcohol and the solution was kept in a vacuum desiccator. After several days crystal foci appeared and on stirring with 80% ethyl alcohol the mass quickly solidified and yielded 27 g. of a new sugar, d-glucoheptulose, showing $[\alpha]_D$ +66, without mutarotation. The sugar was recrystallized several times, to constant rotation, by dissolving it in a small amount of water and adding alcohol or glacial acetic acid. It tastes quite sweet. It crystallizes very readily as well-formed prisms of m. p. 171–174°, after softening at 167°. It is anhydrous, does not lose weight on heating at 100° under reduced pressure in the presence of phosphorus pentoxide, and its analysis corresponds to the formula for a heptose, $C_7H_{14}O_7$. The combustion of 0.2-g. samples gave C, 39.81 and 39.72; H, 6.75 and 6.86; calcd.: C, 40.00; H, 6.67. The pure sugar showed $[\alpha]^{20}_D$ +67.46 in 2.5% aqueous solution and 67.66 in 10% solution; hence $[\alpha]^{20}_D = 67.4 + 0.027\ C$ (where C is concentration) in this range. Decrease of temperature increases the rotation and the formula $[\alpha]^t_D = +67.4 + 0.0278 - 0.027(t-20)$ applies over the range t = 15–30°. Since d-glucoheptulose and d-sorbose are similar in configuration for carbons 3, 4 and 5, it is interesting to note that they are much alike in the ease of crystallization, absence of mutarotation, and the influence of concentration and temperature on their rotations. The dextrorotation of d-sorbose ($[\alpha]_D$ +43) increases with concentration and decreases with rise of temperature.[14] For the mercury yellow line the $[\alpha]^{20}_{578}$ value of d-glucoheptulose is +70.28 in 2.5% solution and for the mercury green line $[\alpha]^{20}_{546.1}$ +79.5 and $[\alpha]^{29.3}_{546.1}$ +79.11 in 2.5% solution.

In the first experiment it was possible to obtain the ketose in pure form, unmixed with d-a-glucoheptose, but in subsequent preparations the two sugars were obtained as a crystalline mixture, due probably to the existence of crystal nuclei of the ketose in the laboratory. The separation of the ketose from this mixture is best accomplished by the oxidation of the aldose with bromine water containing barium benzoate,[15] which leaves the ketose largely unaffected. The precise directions may be omitted, as they have been published for the similar separation of lactose and lactulose by Montgomery and Hudson.[12] The yield of purified ketose when the bromine oxidation step was included in the procedure was about 30% of the weight of the original d-a-glucoheptose.

d-Glucoheptulose is not fermented by baker's yeast. It reduces Fehling's solution on heating and yields 87.6% of the weight of cuprous oxide that is produced by an equal quantity of anhydrous d-glucose. It is not oxidized by the hypoiodite reagent and is therefore a ketose. It gives a blue color in the orcin test, stronger than that produced by d-xylose and weaker than that shown by d-a-glucoheptose. With phloroglucin the same order of color development was found. The ketose also gives positive Seliwanoff and Pinoff tests, as does fructose, while the aldoses do not develop color in these tests; the intensity of the color was much greater for fructose than for *d*-α-glucoheptulose.

Identity of the Osazones of *d*-Glucoheptulose and *d*-α-Glucoheptose.—The osazone of the ketose was prepared by heating a solution of 5 g. of sugar, 15 cc. of phenylhydrazine, 10 cc. of glacial acetic acid and 50 cc. of water for five hours on the steam-bath. After twenty-four hours' standing in the ice box, a good crop of yellow needle crystals was

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[14] Tollens and Smith, *Ber.*, 33, 1289 (1900). Their measurements were upon the levorotatory *l*-sorbose. Bertrand and Nitzberg (Ref. 6, first article) have called attention to the marked resemblance of their a-glucoheptulose (which may now be designated *l*-glucoheptulose) to *l*-sorbose.

[15] Hudson and Isbell, THIS JOURNAL, 51, 2225 (1929).

obtained, weighing 5.5 g. after washing with warm water, 95% alcohol and ether and drying. It was purified by dissolving it in 500 cc. of hot absolute alcohol, treating the solution with decolorizing carbon and keeping it in the ice chest for several days. Anal. combustions of samples weighing 0.2 to 0.3 g. showed C, 58.40 and 58.63; H, 6.32 and 6.36; N (Dumas), 14.43 and 14.25. Calcd. for $C_{19}H_{24}O_5N_4$: C, 58.76; H, 6.19; N, 14.43. The melting point was 194–195° with decomposition after darkening at 185–189°. A solution of 0.4 g. of osazone in 10 cc. of pyridine and 15 cc. of absolute alcohol showed $[\alpha]_D^{20}$ −5.3 two minutes after preparation, +9.6 after two and three-fourths hours and +35.0 final (ninety-six hours).

The osazone of d-a-glucoheptose was prepared similarly and recrystallized twice. Anal. N (Dumas), 14.64; calcd. 14.43. The melting point was 194–195° with decomposition after darkening at 189–190°. A solution of 0.4 g. of osazone in the usual pyridine–alcohol mixture showed $[\alpha]_D^{20}$ −1 two minutes after preparation, +9 after 2.9 hours and +35.6 final (ninety-six hours). A mixture of the two osazones melted at 194–195° with decomposition after darkening in the usual manner. These data show that the two osazones are the same chemical compound, namely, d-glucoheptose osazone, according to the usual tests that are applied to osazones.[16]

These tests have been supplemented by one which Montgomery and Hudson[12] have lately suggestedin connection with the proof of the identity of the anhydro-osazone from lactose and lactulose, namely, the thermodynamic criterion that the solubility of a mixture of two pure samples of the same chemical substance has the same value as the solubility of either sample alone. This test, which is analogous to the mixed melting point test of substances which do not decompose on melting, is rigorous for osazones because there is no decomposition at the temperature of the solubility measurement, whereas the decomposition that occurs on melting invalidates, from the standpoint of thermodynamic theory, tht strict applicability of the mixed melting point test for most osazones. The solubility of *d*-α-glucoheptose osazone in acetone at 20° from undersaturation was 0.0806 g. per 25 cc. of acetone, from supersaturation 0.0814 g.; that of *d*-glucoheptulose osazone was 0.0796 g. from undersaturation and 0.0793 g. from supersaturation, and the solubility of a mixture of the two osazones was 0.0794 g. from undersaturation and 0.0792 g. from supersaturation. Equilibrium was attained in twenty-four to forty-eight hours. This is decisive proof that the two osazones are identical because if such were not the case the mixed solubility would be of the order $0.081 + 0.079 = 0.160$ g. This method is highly recommended in the case of substances for which the mixed melting point test is not theoretically sound because of decomposition on melting or other complications.

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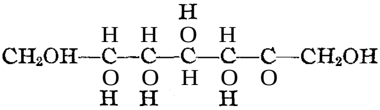
[16] Bertrand and Nitzberg (Ref. 6, first article) state that the osazone of their ketose is identical with *d*-α-glucoheptose osazone but they make no mention of the rotations of the two substances. It seems quite unlikely from the results of the present investigation that the two osazones can be identical. It is to be expected that they are enantiomorphous substances and that the osazone of Bertrand and Nitzberg's ketose, *l*-glucoheptulose, will show a rotation equal to that of d-glucoheptose osazone but of opposite sign.

The author wishes to thank the Medical Fellowship Board of the National Research Council for the award of a fellowship which made possible the carrying out of this research. He also expresses his deep indebtedness to Dr. C. S. Hudson for many valuable suggestions.

Summary

A new crystalline ketose, d-glucoheptulose, of configuration



$$CH_2OH-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{HO}{C}}-\underset{OH}{\overset{H}{C}}-\underset{O}{C}-CH_2OH$$

has been synthesized from d-a-glucoheptose by use of the procedure which Montgomery and Hudson have recently developed for the synthesis of ketoses from aldoses through the Lobry de Bruyn rearrangement. It proves to be the optical enantiomorph of the ketose which Bertrand and Nitzberg recently made through the action of the sorbose bacterium upon a solution of a-glucoheptitol and their ketose is accordingly *l*-glucoheptulose. The rotation of d-glucoheptulose, which does not exhibit mutarotation, is near the value that was predicted by the rotatory relations developed by Hudson. The existence of this ketose, of the calculated rotation, is strong evidence that Hudson's calculation of +67 for the $[\alpha]_D$ value of an unknown a-d-glucose, of the 1,A = 1,4-ring type, is substantially correct.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WEST VIRGINIA UNIVERSITY]

ESTERS OF CYCLOHEXYLRESORCINOL AND PARA-CYCLOHEXYLPHENOL[1]

BY VIRGIL GREENE LILLY AND C. E. GARLAND

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In view of the excellent germicidal properties of some of the alkyl and aryl substituted hydroxy derivatives of benzene[2] and their general low toxicity, some esters, of the salol type, have been prepared using cyclohexylresorcinol[2,3] and *p*-cyclohexylphenol, with a hope that they may prove of therapeutic value.[4]

In general, esters of cyclohexylresorcinol are rather difficult to prepare, while those of p-cyclohexylphenol are less so. Cyclohexylresorcinol does

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[1] This communication is an abstract of part of a thesis submitted by Virgil Greene Lilly in partial fulfilment of the requirements for the degree Master of Arts in Chemistry at West Virginia University.

[2] For a list of important contributions see Bartlett and Garland, THIS JOURNAL, 49, 2098 (1927).

[3] Philips, U. S. Patent 1,650,036.

[4] Kursanoff, *Ann.*, 318, 309 (1901); Wuyts, Bull. *soc. chim. Belg.*, **26**, **304** (1912); Schrauth and Görig, *Ber.*, **56**, 1900 (1923); v. Braun, *Ann.*, **472**, 61 (1929).

not form a crystalline salt when treated with sodium hydroxide, or when cyclohexylresorcinol is dissolved in an indifferent solvent and treated with metallic sodium, but gives a red mass of horn-like consistency. In many of the esterification reactions attempted it appeared to undergo a kind of polymerization to give tar-like products which we were unable to purify. The sodium salt of *p*-cyclohexylphenol crystallizes easily from aqueous solution in thin plates. The potassium salt does not crystallize readily.

Three general methods were used to prepare the esters, as follows: the Schotten–Baumann reaction, the action of thionyl chloride or other condensing agents, and the action of acid chlorides upon the dry alkali phenolates.

The cyclohexylresorcinol and cyclohexylphenol used in preparing the following esters were supplied through the courtesy of Dr. R. R. Read, of Sharpe and Dohme, Baltimore, to whom the thanks of the authors are due.

Experimental Part

Cyclohexylresorcinol Dibenzoate, $(C_6H_3)(C_6H_{11})\cdot(C_7H_5O_2)_2(1,2,4)$.—To 100 cc. of 10% potassium hydroxide was added 10 g. of cyclohexylresorcinol, which dissolved to a red wine color. Fifteen and three-tenths grams of benzoyl chloride was added gradually, the reaction mixture being stirred vigorously during the course of the reaction, which was complete within twenty minutes. A heavy yellow oil formed which settled to the bottom. The supernatant liquid was decanted and the heavy oily product repeatedly washed with water. This oil did not deposit crystals, so it was dissolved in a small quantity of hot alcohol, from which the solid product readily separated on cooling. After two recrystallizations from alcohol the white plate crystals melted sharply at 88°. The crystals have a pleasant aromatic odor; yield, 60%.

Anal. Calcd. for $C_{26}H_{24}O_4$: C, 78.00; H, 6.00. Found: C, 77.81, 77.96; H, 5.51, 6.19.

p-Cyclohexylphenol Salicylate, $C_6H_4(C_6H_{11})\cdot(HOC_6H_4COO)(1,4)$. Method I.—Eight grams of well dried sodium *p*-cyclohexylphenolate and 12 g. of sodium salicylate together with 30 cc. of phosphorus oxychloride and 10 g. of finely powdered sodium chloride were heated in a balloon flask[6] on a sand-bath for an hour at 130°. The heat was then removed and the flask allowed to cool to room temperature. The reaction mixture was extracted with an equal mixture of ethyl and methyl alcohols. White crystals separated from the alcoholic solution, which melted at 103.5'. Results by this method are very uncertain and usually the yield is very small.

Method 11.—Twenty grams of cyclohexylphenol and the theoretical amount of salicylic acid were refluxed with an excess of thionyl chloride on a water-bath for two hours. The excess thionyl chloride was decomposed with cold water, the residue well washed and dissolved in alcohol. The crystalline product after further purification melted at 103.5°. A mixed melting point of the products from Methods I and II gave 103°; yield, 25%.

Anal. Calcd. for $C_{19}H_{20}O_3$: C, 77.03; H, 6.75. Found: C, 77.09, 76.94; H, 7.10, 6.91.

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[5] U. S. Patent 1,606,171.

p-Cyclohexylphenol Hydrocinnamate, $C_6H_4(C_6H_{11})\cdot(C_6H_5CH_2CH_2COO)(1,4)$.—The acid chloride of hydrocinnamic acid was prepared by the method of McMaster and Ahmann.[6] Hydrocinnamic acid was refluxed with an excess of thionyl chloride for two hours, the excess thionyl chloride distilled off, and the acid chloride purified by vacuum distillation. (Other acid chlorides used in this investigation were prepared in a similar manner.)

Twenty grams of sodium cyclohexylphenolate and 17 g. of hydrocinnamoyl chloride were well stirred for ten minutes and at the same time gently warmed. The product was repeatedly washed with water and the residue dissolved in hot alcohol. On cooling, fine needle-like crystals rapidly separated out. On recrystallization the product melted at 74°; yield, 33%.

Anal. Calcd. for $C_{21}H_{24}O_2$: C, 81.82; H, 7.79. Found: C, 81.39, 81.57; H, 7.88, 7.84.

p-Cyclohexylphenol m-Nitrobenzoate, $C_6H_4(C_6H_{11})(O_2NC_6H_4COO)(1,4)$.—The acid chloride of *m*-nitrobenzoic acid and the calculated amount of well dried sodium cyclohexylphenolate were warmed together for ten minutes, the reaction mixture washed repeatedly with water and dissolved in hot alcohol. The crystals on further purification melted at 114°. Analysis was by the method of Knecht and Hibbert.[7]

Anal. Calcd. for $C_{19}H_{19}O_4N$: N, 4.31. Found: N, 4.50, 4.32.

p-Cyclohexylphenol p-Nitrobenzoate, $C_6H_4(C_6H_{11})(O_2NC_6H_4COO)1,4$.—Three grams of p-cyclohexylphenol and the calculated amount of *p*-nitrobenzoic acid were heated with 10 g. of thionyl chloride and 5 g. of phosphorus trichloride for an hour on a water-bath. The excess acid chlorides were decomposed with water and the residue was crystallized from alcohol. The first crop of crystals was rejected and the second portion after repeated recrystallizations melted at 137°; yield, 15%.

Anal. Calcd. for $C_{19}H_{19}O_4N$: N, 4.31. Found: 4.37, 4.41.

Summary

The following salol type esters of cyclohexylresorcinol and *p*-cyclohexylphenol have been prepared and described: (1) cyclohexylresorcinol dibenzoate, (2) p-cyclohexylphenol salicylate, (3) p-cyclohexylphenol hydrocinnamate, (4) p-cyclohexylphenol m-nitrobenzoate and (5) *p*-cyclohexylphenol *p*-nitrobenzoate.

MORGANTOWN, WEST VIRGINIA

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[6] McMaster and Ahmann, THIS JOURNAL, 50, 145 (1928).

[7] "New Reduction Methods in Volumetric Analysis," Longmans, Green, 1910, and *J. Soc. Chem. Ind., 39,* 87 (1920).

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY AND TOXICOLOGY, YALE UNIVERSITY MEDICAL SCHOOL]

LOCAL ANESTHETICS DERIVED FROM DIALKYLAMINOPROPANEDIOLS. I. PHENYLURETHANS

BY T. H. RIDER

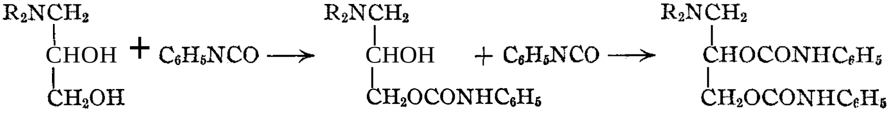
RECEIVED FEBRUARY 7, 1930 PUBLISHED MAY 8, 1930

A great majority of the more recently synthesized local anesthetics are *p*-aminobenzoates of suitable alcohols. In view of the structural similarity between phenylcarbamic acid esters (I) and *p*-aminobenzoic acid esters (II), it is surprising that the field of the phenylurethans

(I) $C_6H_5NHCOO—$ (II) $NH_2C_6H_4COO—$

has not been more generally investigated from the standpoint of the determination of their local anesthetic properties. This is perhaps due to the rather unsatisfactory properties of the urethans studied by Fromherz[1] and Bonar and Sollman.[2] The only other references to this type of compound are found in patents[3] which give no data on pharmacological properties.

In a previous communication,[4] a general preparation of dialkylaminopropanediols ($R_2NCH_2CHOHCH_2OH$) was described and attention was called at that time to their probable usefulness in the synthesis of certain types of local anesthetics. This paper, the first of a series devoted to the preparation of anesthetics derived from these intermediates, deals specifically with the mono- and diphenylurethans, prepared by the action of phenyl isocyanate on the dialkylaminopropanediols



$$\begin{array}{l}R_2NCH_2\\ \quad|\\ \quad CHOH\\ \quad|\\ \quad CH_2OH\end{array} + C_6H_5NCO \longrightarrow \begin{array}{l}R_2NCH_2\\ \quad|\\ \quad CHOH\\ \quad|\\ \quad CH_2OCONHC_6H_5\end{array} + C_6H_5NCO \longrightarrow \begin{array}{l}R_2NCH_2\\ \quad|\\ \quad CHOCONHC_6H_5\\ \quad|\\ \quad CH_2OCONHC_6H_5\end{array}$$

The di-urethans are formed with comparative ease when the alcohols are reacted with two molecular proportions of phenyl isocyanate, The mono-urethans, however, are more difficult to obtain, since there is a decided tendency of the β-hydroxyl group of the dialkylaminopropanediols to react, even in the presence of an excess of the alcohol, yielding the di-urethans where the mono-urethans might be expected. In isolating the product from the reaction mixture, the obvious procedure would be to extract with dilute acid and liberate the free base by the addition of alkali. While it is possible to isolate the di-urethans in this manner, the mono-urethans are decomposed by alkali before they can be isolated. These considerations without doubt explain the error in German Patent 272,529,

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[1] Fromherz, *Arch. Exptl. Path. Pharmakol.*, *76*, **257 (1914).**

[2] Bonar and Sollman, J. *Pharmacol.*, 18, *467* **(1921).**

[3] German Patents **272,529** and 364,038.

[4] Rider with Hill, THIS JOURNAL, **52, 1528 (1930).**

purporting to cover the mono-phenylurethan of diethylaminopropanediol. The free base only was prepared, and the preparation of this compound is poorly described by the patent. The only property given is the melting point, 106.5°, which is identical with that of the true diurethan as isolated by the writer. It seems certain, therefore, that this compound was isolated, rather than the one claimed.

In the preparation of these compounds the author has prepared for the first time di-n-butylaminopropanediol according to the procedure outlined in a previous paper.[4] In most cases the hydrochlorides of the urethans were prepared without isolating the free bases, and little consideration has been given to improving the yields, which range from 25–60%. Only those compounds whose pharmacological properties are satisfactory merit a more detailed study.

Experimental

Di-*n*-butylaminopropanediol.—Equimolecular proportions of di-n-butylamine and glycidol were mixed and heated on a steam-bath for two hours. The reaction mixture was distilled under reduced pressure; di-n-butylaminopropanediol distils at 127" (3 mm.). The yield is 90% of the theoretical.

Anal. Calcd. for $C_{11}H_{25}O_2N$: N, 6.90. Found: N, 6.91, 6.93.

Hydrochlorides of Mono-phenylurethans of Dialkylaminopropanediols.—An ethereal solution of one mole of phenyl isocyanate is rapidly mixed with an ethereal solution of the dialkylaminopropanediol. The reaction mixture is refluxed until the characteristic odor of phenyl isocyanate disappears, this being taken as a criterion of the completion of the reaction. After cooling of the reaction mixture, the hydrochloride is precipitated, usually as an oil, by the addition of an ethereal solution of dry hydrogen chloride. The ether is decanted and the hydrochloride is recrystallized from acetone. The solubility of the urethans in acetone increases with the molecular weight, necessitating the use of a mixture of acetone and ethyl acetate for the recrystallization of the higher homologs. No difficulty is found in obtaining a crystalline solid when seed crystals are available, although the first isolation sometimes proves difficult. The urethan of the amyl homolog is exceedingly difficult to purify, since it must be thrown out of an ethyl acetate solution with ether, or recrystallized by evaporating a water solution. Either procedure gives a product of somewhat varying properties. The compounds prepared are as follows.

TABLE I

$C_6H_5NHCOOCH_2CHOHCH_2NR_2 \cdot HCl$ COMPOUNDS

R	Formula	Nitrogen, % Calcd.	Nitrogen, % Found		Chlorine, % Calcd.	Chlorine, % Found		M. p., °C.
Methyl	$C_{12}H_{18}O_3N_2HCl$	10.2	10.1	10.0	12.9	12.8	13.0	138–140
Ethyl	$C_{14}H_{22}O_3N_2HCl$	9.26	9.3	9.1	11.7	12.0	11.8	135
n-Propyl	$C_{16}H_{26}O_3N_2HCl$	8 47	8.4	8.5	10.7	10.5	10.9	163–164
Isobutyl	$C_{18}H_{30}O_3N_2HCl$	7.81	7.8	7.9	9.89	9.8	9.9	125–127
n-Butyl	$C_{18}H_{30}O_3N_2HCl$	7.81	7.8	7.8	9.89	9.7	9.7	128–129
***n*-Amyl**	$C_{20}H_{34}O_3N_2HCl$	7.25	7.1	7.4	9.18	9.0	9.4	101–103
Piperidino (NR_2)	$C_{15}H_{22}O_3N_2HCl$	8.90	...	...	11.3	11.3	11.8	176–177

Hydrochlorides of Diphenylurethans of Dialkylaminopropanediols.—The diphenylurethans are prepared in a manner entirely analogous to that of the mono-phenylurethans by using two molecular proportions of phenyl isocyanate. The di-urethans are more soluble in acetone than the corresponding mono-urethans but are crystallized in the same manner. The following hydrochlorides of the di-phenylurethans of dialkylaminopropanediols have been prepared.[5]

TABLE II

$C_6H_5NHCOOCH_2CH(OCONHC_6H_5)CH_2NR_2 \cdot HCl$

R	Formula	Nitrogen, % Calcd.	Nitrogen, % Found		Chlorine, % Calcd.	Chlorine, % Found		M. p., °C.
Ethyl	$C_{21}H_{27}O_4N_3HCl$	9.96	10.1	9.8	8.4	7.9	8.3	109
n-Propyl	$C_{23}H_{31}O_4N_3HCl$	9.36	9.4	9.2	7.9	8.1	8.0	183–188
Isobutyl	$C_{25}H_{35}O_4N_3HCl$	8.80	8.75	8.85	7.4	7.5	7.4	116–118
Piperidino (NR_2)	$C_{22}H_{27}O_4N_3HCl$	9.1	....		8.2	8.1	8.2	197–198

The Free Base of the Di-phenylurethan of Diethylaminopropanediol.—The hydrochloride, prepared as above described, was dissolved in water, an excess of alkali added, the product separated by means of ether extraction, the ethereal solution dried over anhydrous sodium sulfate, filtered and evaporated. The residue was recrystallized from high-boiling petroleum ether, yielding crystals of the di-phenylurethan of diethylaminopropanediol; melting point 106.5°.

Anal. Calcd. for $C_{21}H_{27}O_4N_3$: N, 10.9. Found: N, 10.7, 10.9.

Pharmacological Properties.—The following table will serve roughly to evaluate the strength of the two series of compounds as local anesthetics. The tests were made with a 1% solution of the hydrochloride in distilled water. The time in minutes required for the production of sensory and motor anesthesia in the exposed sciatic nerve of the frog is given in the second and third columns. The fourth column gives the duration of anes-

TABLE III

ANESTHETIC PROPERTIES

Compound	Time of onset of anesthesia, min. Sensory	Time of onset of anesthesia, min. Motor	Duration of anesthesia, min. Cornea
Cocaine	4	14	26
Mono-urethans			
R = methyl	30	52	Incomplete
R = ethyl	25	49	15
R = *n*-propyl	14	31	26
R = n-butyl	6	23	42.6
R = isobutyl	8	26.5	50
R = n-amyl	6	13.5	65[a]
NR_2 = piperidino	9.5	35	Incomplete
Di-urethans			
R = ethyl	18	47	30
R = n-propyl	16	55	42
R = isobutyl	10	36	41
NR_2 = piperidino	5	38	54

[a] Using a solution of 0.5 of 1%.

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[5] The methyl and amyl homologs were also prepared, but not purified, the methyl compound being hygroscopic and the weakest anesthetic of the series, while the hydrochloride of the amyl compound is practically insoluble in water.

thesia after a one-minute application of the solution to the cornea of the rabbit.

From the table it may be seen that the compounds are comparatively much more effective on the cornea than on the exposed nerves. The isobutyl homolog of the series of mono-urethans, which is approximately twice as effective on the cornea as cocaine, has a much lower apparent toxicity, the minimum fatal dose for white mice, injected subcutaneously, being 1500 mg. per kilo.

Both the study of the production of anesthesia and that of the toxicity are complicated, more especially in the di-urethan series, by the tendency of the higher homologs to precipitate proteins. A further study of this feature, together with a more complete pharmacological report, will be published elsewhere.

Since these urethans show such promising local anesthetic properties, the author proposes to extend this field through the preparation of other urethan combinations of the dialkylaminopropanediols and the urethans of other amino alcohols.

Summary

The mono- and di-phenylurethans of a number of dialkylaminopropanediols have been prepared and have been shown to have interesting local anesthetic properties.

Di-n-butylaminopropanediol has been prepared for the first time.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, COLUMBIA UNIVERSITY]

METHYL ISOPROPYL THIOINDIGOID DYES FROM PARA-CYMENE. I. DYES FROM AMINOCYMENE[1]

BY A. W. HIXSON AND W. J. CAUWENBERG

RECEIVED FEBRUARY 8, 1930 PUBLISHED MAY 8, 1930

Introduction

The number of known sulfur-containing indigoid dyes is very great[2] and their commercial importance is steadily increasing, as shown by the introduction of new colors of this series into the industry. These dyes are of particular interest due to the great effect of substitution on the color. Whereas the derivatives of indigo do not differ greatly in color, those of thioindigo cover almost the entire range of the spectrum. A survey of the literature showed that practically all of the simple benzene derivatives

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[1] This communication is an abstract of a portion of a thesis submitted by W. J. Cauwenberg in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, to the Faculty of Pure Science of Columbia University.

[2] Truttwin, "Enzyklopadie der Kupenfarbstoffe," Springer, Berlin, 1920.

have been converted into thioindigo dyes but that no derivative containing an isopropyl group has been used. It was thought that *p*-cymene, which is produced in large quantities as a by-product in the sulfite paper industry, could be used as a starting material for the production of methyl isopropyl thioindigo dyes.

The simplest thioindigo was first prepared by Friedländer[3] by the application of the Badische modification of the Heumann synthesis for indigo to thiosalicylic acid. Condensation with chloro-acetic acid gives the desired grouping, namely, a-carboxyphenylthioglycolic acid. In the preparation of highly substituted derivatives, anilines containing the desired groups are usually employed. The ortho sulfur atom is introduced through a sulfonic acid group or by the Hofmann reaction. The amino group is then converted to the carboxyl by the Sandmeyer reaction and hydrolysis.

A very important industrial method for the production of *o*-aminophenylthioglycolic acids has been introduced by Herz.[4] Aromatic amines with an unsubstituted ortho position are condensed with sulfur chloride and the condensation product is caused to react with chloro-acetic acid. The resulting product is the desired substituted o-aminophenylthioglycolic acid. The amine is converted by the Sandmeyer reaction to the nitrile, which is then hydrolyzed and condensed to the thionaphthene. These compounds are employed to prepare a large number of sulfur-containing indigoid dyes. They may be oxidized to give thioindigos or condensed with isatin through the alpha or beta oxygen to give Thioindigo Scarlet or Ciba Violet derivatives and with acenaphthenequinone to give substituted Ciba Scarlets.

This paper presents the preparation of methyl isopropyl thioindigoid dyes from aminocymene by the sulfur chloride condensation method. 4-Methyl-6-chloro-7-isopropyl-3-hydroxythionaphthene produced by this method was condensed with isatin and acenaphthenequinone. The relative fastness properties are reported using the commercial dye made from o-toluidine as a standard. Spectrum analyses are also reported and the effect of the isopropyl group is a shift of nine millimicrons in the direction of the longer wave lengths.

The method followed in the synthesis of these dyes may be represented as indicated in the Flow Sheet.

Experimental Part

Preparation of Materials.—The cymene used for this work was prepared by steam distillation of the spruce turpentine after two hours aeration at room temperature in the presence of aqueous caustic. At first the distillate was colorless and contained 37% of oil by volume. The distillation was continued until the oil had a slight yellow color and the rate had fallen to 17% oil. The average yield was 67.5%. A distillation test

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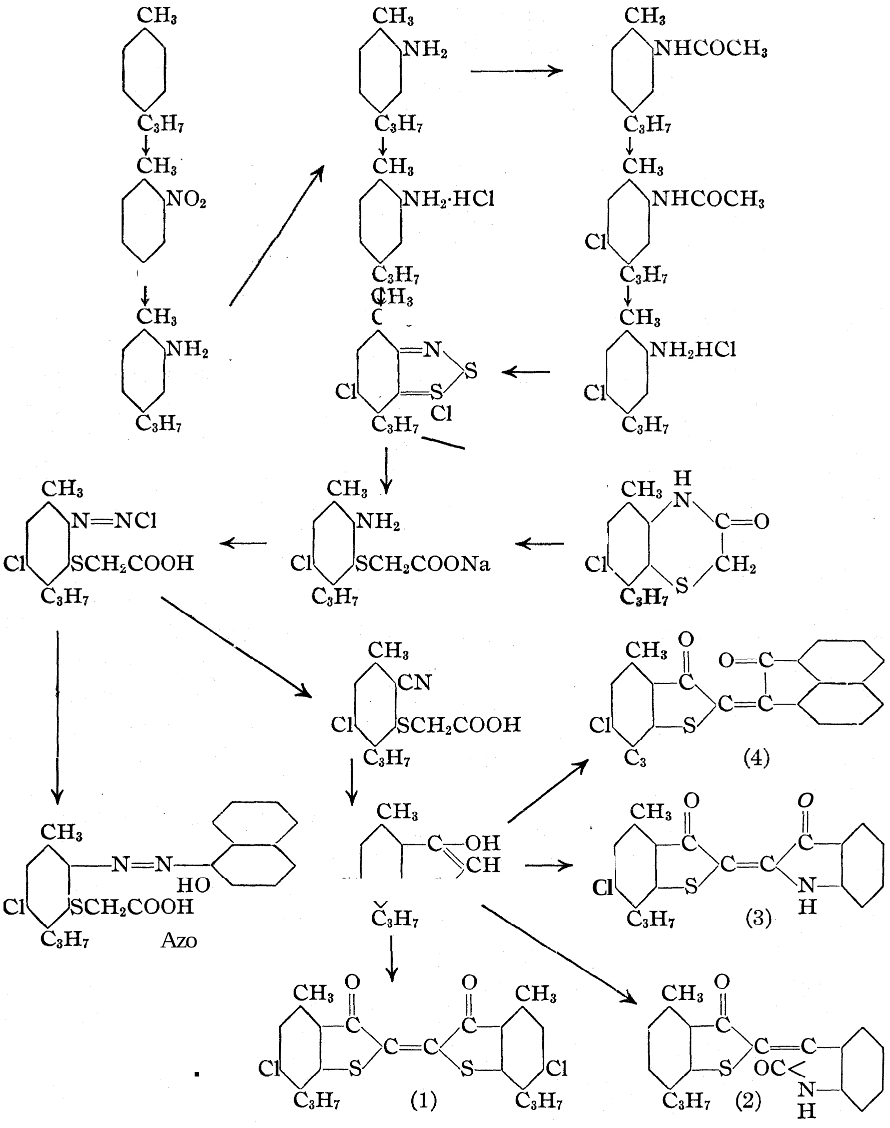
[3] Friedländer, *Ber.*, **39,** 1060 (1906).

[4] Herz. German Patent 360.690.



FLOW SHEET

showed that 80% of the oil distilled between 173.8–177.5°. The oil was not further purified for nitration.

The nitration of cymene was carried out as outlined by Demonbreun and Kremers.[5] The crude nitrocymene was purified by distillation at 6 mm. and the fraction boiling between 105–127° was separated. The greater portion of this fraction boiled between 112–120°. The yield was 54.6%.

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[5] Demonbreun and Kremers, *J. Am. Pharm. Assocn.*, *12,* 296 (1923).

Aminocymene was prepared by the standard iron reduction with a yield of 88.8%. Since the amine was wanted as the hydrochloride, it was dissolved in benzene and precipitated with hydrochloric acid gas.

Condensation Product of Aminocymene and Sulfur Chloride.—Sulfur chloride (210 g.) was placed in a one-liter flask equipped with an agitator, reflux condenser and gas outlet. After cooling to 20°, 30 g. of aminocymene hydrochloride was added as fast as it could be incorporated by the agitator. The mass was stirred for three hours under these conditions and allowed to stand overnight at room temperature. The next morning it was heated to 50° and held until the evolution of hydrochloric acid had ceased. An equal volume of benzene was added and cooled to 30°. The condensation product crystallized in orange-red plates. It was separated by filtration and washed free from sulfur chloride with dry benzene. The cake was dried *in vacuo* at 50° and the yield was 38 g. or 84% of the theoretical based on $C_{10}H_{11}NS_2Cl_2$.

Since the condensation mass became very thick during the heating period and required constant attention, the amount of sulfur chloride was increased to ten parts This increase gave a much smoother reaction but a smaller yield, 77.5%.

The compound is a bright orange-red powder which slowly changes to brown. It is hydrolyzed by water with the removal of one chlorine atom, and by alcohol, in which the hydrolysis product is soluble. It is soluble in benzene, toluene, acetic acid and other organic solvents with which it does not react. It was purified by dissolving in glacial acetic acid and precipitating with ether. The purified product gave the following analysis.

Anal. Calcd. for $C_{10}H_{11}NS_2Cl_2$: S, 22.82; Cl, 25.35; Cl/S, 1.11. Found: S, 22.08; Cl, 24.52; Cl/S, 1.11.

The material charred at 120° without melting.

The filtrate and benzene washings from the condensation was fractionated and 43% of the sulfur chloride was recovered. The total benzene recovery was 91%.

5-Chloro-2-aminocymene-3-thioglycolic Anhydride.—The sulfur chloride condensation product (16.8 g.) was added to 120 cc. of water at 10°. The suspension was well agitated for two hours, during which time the material turned to a gray precipitate with a colorless supernatant liquor. The hydrolysis product was separated by filtration and washed free of acid with cold water. The cake was suspended in 150 cc. of cold water and 25 cc. of a 40% caustic soda solution was added. A neutralized solution of 8.5 g. of chloro-acetic acid in 50 cc. of water was added and it was heated to 45°. After one-half hour at this temperature the yellow solution was filtered from solid impurities and acidified with sulfuric acid. The precipitated acid was converted to the anhydride by heating to 70°. It was filtered and washed first with water and then with dilute ammonia. The yield was 12.1 g. or 79% of the theoretical.

The material was purified by crystallization from benzene. The product was obtained as fine white crystals soluble in organic solvents, insoluble in water, dilute acids and alkalies. It melted at 159.0–159.8°.

Anal. Calcd. for $C_{12}H_{14}ONSCl$: Cl, 13.92; S, 12.57; N, 5.48. Found: Cl, 13.89; S, 12.33; N, 5.50.

The anhydride ring can be opened to the acid by heating with 40% caustic soda solution (containing an amount of caustic equal to the weight of anhydride) at 120°. The anhydride first melts and then solidifies as the sodium salt.

Allocation of the Chlorine Atom Introduced during the Sulfur Chloride Condensation.—Herz[4] states that if the amine contains an unsubstituted para position, a chlorine atom will be introduced during the sulfur chloride condensation. Analysis of the condensation product showed the presence of two chlorine atoms, one of which could not be removed by hydrolysis. The thioglycolic anhydride indicated chlorination either in the nucleus or the side chain. The anhydride ring was opened with caustic soda as previously described but the time was extended thirty minutes. The salt was dissolved in water, filtered from insoluble impurities and converted back to the anhydride. Chlorine analysis showed that the substitution was in the nucleus.

If the above substitution theory is correct, then p-chloro-aminocymene should give the same condensation product and anhydride. This procedure was thought to be the best method of attack for the solution of this problem. The *p*-chloro-aminocymene was prepared by the method reported by Wheeler and Giles[6] and converted to the thioglycolic anhydride. The anhydrides obtained from aminocymene and p-chloro-aminocymene were identical, as shown by analyses, melting point and mixed melting point. The position of the chlorine atom is therefore established, being assigned to the 5-position or para to the amino group.

TABLE I

SUMMARY OF THE ANALYSES OF THE ANHYDRIDES

	Cl	*S*	N	**M. p., °C.**
Calcd.	13.92	12.57	5.48	......
Aminocymene	13.89	12.33	5.50	159.0–159.8
Chloro-aminocymene	13.90	12.50	..	159.8
Mixed	...	...	..	159.8

Diazotization of 5-Chloro-2-aminocymene-3-thioglycolic Acid.—A solution of the sodium salt which was obtained from an experiment similar to the one described under the preparation of the anhydride was filtered and to the clear solution, which contained 0.045 mole, was added 3.45 g. of sodium nitrite dissolved in 20 cc. of water. This solution was added through a dropping funnel to 50 cc. of water, 50 g. of ice and 15 cc. of hydrochloric acid. The temperature was held at 10° by means of an external ice-bath. The diazo solution was filtered and diluted to 500 cc.

Efficiency.—A @-naphthol solution containing 0.00139 mole as the sodium salt was titrated with the above diazo solution. Twenty-one cubic centimeters of the diazo solution was required, which gives an efficiency of 73.4%.

Azo Dye.—Two hundred and fifty cubic centimeters of the diazo solution after neutralization was added to **a** cold solution of 2.5 g. of @-naphthol in 100 cc. of water plus enough caustic soda to give a clear solution. The dye formed immediately and was coagulated with acetic acid. It was separated by filtration, washed and dried. The yield was 7.0 g. or 99.4% of the theoretical. The crude dye was crystallized from acetic acid and the pure compound was obtained as long red needles with a metallic reflex.

Anal. Calcd. for $C_{22}H_{21}O_3N_2SCl$: Cl, 8.27; S, 7.48. Found: Cl, 8.28; S, 7.50.

Preparation of 2-Cyano-5-chlorocymene-3-thioglycolic Acid and **4-Methyl-6-chloro-7-isopropyl-3-hydroxythionaphthene.**—The conversion of the aminophenylthioglycolic acid to the cyano derivative may be applied to the sodium salt obtained either from the anhydride or from the chloro-acetic acid condensation. The reaction is very sensitive to sulfite, sulfide and hydroxyl ions. The sulfite and sulfide ions were

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[6] Wheeler and Giles, THIS JOURNAL, 44, 2605 (1922).

removed by salting out the sodium salt with sodium chloride at 10° and washing the cake with cold saturated brine. The hydroxyl-ion concentration was adjusted by the addition of dilute acetic acid.

A solution (1.5 liters) containing 0.31 mole of the sodium salt prepared from 0.392 mole of the sulfur chloride condensation product was cooled to 10° and saturated with sodium chloride. The precipitated salt was filtered and washed with cold saturated brine. The washed product was dissolved in warm water and diluted to 765 g. Twenty-five grams of this solution was acidified and converted to the anhydride, which was weighed. It was 10% by weight. The remainder of the solution (740 g. or 0.29 mole) was diazotized by the method previously described. The neutral diazo solution was added to the cyanide and adjusted to PH 6.1 using chlor phenol red as indicator. The reaction mass was heated to 50° and held for thirty minutes. The stirring was stopped and the material allowed to stand overnight at room temperature. The clear supernatant liquor was acidified with hydrochloric acid. The cuprous cyanide and nitrile were separated and the nitrile was extracted with dilute sodium carbonate. The carefully neutralized solution was separated from the precipitated tar and after saturating with sodium chloride the sodium salt of the nitrile separated as long white needles. It was purified by recrystallization from water and converted to the free acid. The nitrile separated as a light tan-colored oil.

Anal. Calcd. for $C_{13}H_{14}O_2NSCl$: S, 11.30. Found: S, 11.76.

The tar which precipitated during the evolution of the nitrogen and contained the greatest portion of the nitrile was isomerized at 80° with dilute caustic soda and transferred to a mechanically agitated apparatus to which was connected a reflux condenser and oil separator. It was refluxed with a 25% sulfuric acid solution and the thionaphthene distilled as a colorless oil which assumed a red color due to atmospheric oxidation. The rate was about 5 g. in eight hours. The yield was 19.5 g. or 39.8% of the theoretical on the diazo salt.

The thionaphthene is a colorless oil heavier than water, in which it is insoluble. It is soluble in organic solvents and caustic soda, with which it forms a sodium salt. It cannot be distilled at atmospheric pressure without decomposition but distils readily at 10 mm. The fraction boiling between 191–193° at 10 mm. was separated for analysis.

Anal. Calcd. for $C_{12}H_{13}OSCl$: S, 13.30. Found: S, 13.31.

An interesting observation was made on this oil. When sealed in glass tubes at atmospheric and 10 mm. pressure and exposed to sunlight the red color of the oil at reduced pressure was discharged in five to seven minutes and after standing in the dark for twelve hours returned to its former intensity. The action of sunlight on vat dyes is generally considered to be a reduction of the dye to the leuco compound. In an atmosphere deficient in oxygen the color of this oil was discharged due to the reduction of the dissolved dye to the colorless leuco.

Dyes from 4-Methyl-6-chloro-7-isopropyl-3-hydroxythionaphthene

4,4-Dimethyl-6,6-dichloro-7,7-di-isopropyl-2,2-*bis*-thionaphthene Indigo. **1.**[7]—Thionaphthene was dissolved in ten parts of 5% caustic soda solution and heated to 60°.[8] One-half part of sulfur was added and the heating continued until the dye was completely precipitated. It was separated by filtration, washed and dried. The yield was quantitative.

The dye was purified for analysis by crystallization from xylene, from which it was obtained as fine red crystals. It is sparingly soluble in high-boiling organic solvents.

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[7] The numbers after the names of the dyes refer to the flow sheet.

[8] Fierz, "Kunstliche Organische Farbstoffe," Springer, Berlin, 1926, p. 461.

Anal. Calcd. for $C_{24}H_{22}O_2S_2Cl_2$: S, 13.42; Cl, 14.88. Found: S, 13.35; Cl, 14.71.

4-Methyl-6-chloro-7-isopropyl-2-thionaphthene-3-indol Indigo. 2.—Thionaphthene (1.76 g.) and isatin (1 g.) were dissolved in 30 cc. of acetic acid[0] and heated to 90°. The catalyst (two drops of hydrochloric acid) was added and held at 90° for thirty minutes. The dye, which separated in fine red crystals, was filtered and recrystallized from xylene. The yield was 1.7 g. or 63%.

Anal. Calcd. for $C_{20}H_{16}NO_2SCl$: S, 8.67; Cl, 9.61. Found: S, 8.65; Cl, 9.41.

4-Methyl-6-chloro-7-isopropyl-2-thionaphthene-2-indol Indigo. 3.—Isatin (1.36 g.) was dissolved in 50 cc. of benzene with 1.9 g. of phosphorus pentachloride to form isatin chloride,[10] which was added to 1.76 g. of thionaphthene dissolved in 200 cc. of benzene at 50°. The violet dye which formed immediately was separated and recrystallized from xylene. The yield was 2.4 g. or 89%.

Anal Calcd. for $C_{20}H_{16}NO_2SCl$: S, 8.67. Found: S, 8.52.

4-Methyl-6-chloro-7-isopropyl-2-thionaphthene-acenaphthene Indigo. 4.—Thionaphthene (0.95 g.) and acenaphthenequinone (0.7 g.) were dissolved in 30 cc. of acetic acid and heated to 90°.[11] Two drops of hydrochloric acid was added and the reaction held at 90" for thirty minutes. The dye was separated and crystallized from xylene with a yield of 1 g. or 64%.

Anal. Calcd. for $C_{24}H_{17}O_2SCl$: S, 7.92. Found: S, 7.82.

Properties of Dyes

Solubility.—These dyes are insoluble in water, dilute acids and alkalies and salts with the exception of alkaline hyposulfite, with which they form the vat.

Fastness.—The relative fastness to light was determined by exposing them for seventy-two hours to an ultraviolet lamp (used less than 200 hours) at a distance of eighteen inches.

The fastness to washing was determined by applying the standard test except that the time was increased from five to ninety minutes.

TABLE II

PROPERTIES OF DYES

No.	Color in H_2SO_4	Color of vat	Color in xylene[a]	Wash test	Fastness to light	Color of crystals
FF"	Green	Yellow	Pink y	Exc.[a]	Bxc.	Red
I	Green	Yellow	Pink y	Good	Exc.	Red
2	R violet	Colorless	Orange	Good	Fair	Orange
3	B green	Yellow	Violet	Exc.	Good	B black
4	Green	Violet	Yellow y	Good	Fair	Red
Azo	Red	......	Yellow	...		Red

[a] y after color in xylene denotes yellow fluorescence. FF is the commercial dye made from o-toluidine. Exc. for excellent.

Spectrum Analyses.—These analyses were made with a Koenig–Martens spectrophotometer using xylene as the solvent.

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[9] German Patent 205,377.

[10] Bezdzik and Friedlander, *Monatsh.*, 29, 377 (1908).

[11] Bezdzik and Friedlander, *ibid.*, 30, 284 (1909).

TABLE III

SPECTRUM ANALYSES OF DYES

No. of dye	FP	1	2	3	4	Azo
Wave length, millimicrons	540	549	503 514	576	478 514	465 496

[a] The value given for FF (Ref. 8, p. 464) is 540.

The authors acknowledge their indebtedness to Dr. B. Kurrelmeyer, Department of Physics, Columbia University, for his helpful suggestions during the spectrum analyses of these dyes.

Summary

1. A number of new sulfur derivatives were prepared from aminocymene.
2. The position of the chlorine atom introduced into the nucleus during the sulfur chloride condensation of aminocymene hydrochloride was determined.
3. A new azo dye was prepared.
4. Four new thioindigoid dyes containing an isopropyl group were prepared.
5. Fastness tests and spectrum analyses of the dyes were made.
6. The effect of the isopropyl group was found to be a shift of nine millimicrons in the direction of the longer wave lengths.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, COLUMBIA UNIVERSITY]

METHYL ISOPROPYL THIOINDIGOID DYES FROM PARA-CYMENE. II. DYES FROM SODIUM CYMENE SULFONATE[1]

BY A. W. HIXSON AND W. J. CAUWENBERG

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Introduction

The original Heumann synthesis of indigo may be applied to thiophenols for the preparation of thioindigo dyes and this method is now employed in the industry on substituted thiophenols. These compounds are usually prepared by the reduction of the corresponding sulfonyl chlorides or by the action of potassium ethyl xanthate on diazotized amines. After condensing with chloro-acetic acid, the substituted phenylthioglycolic acids are internally dehydrated to the thionaphthene derivatives by chloro-sulfonic or sulfuric acids.

The application of this method to sodium cymene sulfonate would produce thioindigoid dyes which are isomeric with those prepared from amino-

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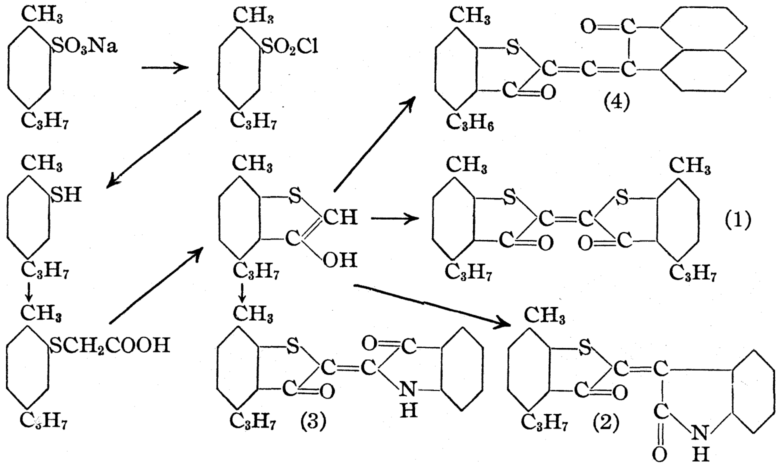
[1] This communication is an abstract of a portion of a thesis submitted by W. J. Cauwenberg in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, to the Faculty of Pure Science of Columbia University.

cymene by the sulfur chloride method.[2] This paper presents the preparation of methyl isopropyl indigoid dyes from sodium cymene sulfonate. 7-Methyl-4-isopropyl-3-hydroxythionaphthe prepared by this method was oxidized to the thioindigo and condensed with isatin and acenaphthenequinone. The relative fastness, properties and spectrum analyses are reported. The method followed in the synthesis of these dyes may be represented as shown in the Flow Sheet.



FLOW SHEET

Experimental Part

Reparation of Materials

The sodium cymene sulfonate prepared according to Hixson and McKee[3] was obtained from the Chemical Engineering Laboratory of Columbia University. It was recrystallized twice from alcohol and dried for eighteen hours at 140°.

Cymene-2-sulfonyl chloride was prepared as outlined by Phillips.[4]

Thiocarvacrol.—This compound was first prepared by Flesch[5] from camphor by the action of phosphorus pentasulfide. Roderburg[6] reported the preparation from the sulfonyl chloride. The method used in this work was an adaptation of the thiophenol process of Adams and Marvel.?

The wet sulfonyl chloride from 25 g. of sodium cymene sulfonate was added slowly to a mixture of 210 g. of ice and 71 g. of sulfuric acid at −5°. Thirty-six grams of zinc dust was introduced, keeping the temperature below 0°. After stirring the mixture for one and one-half hours at 0°, the ice–salt bath was removed and a reflux condenser connected to the Y-tube. The mass was heated to boiling (no vigorous reaction during the

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[2] Hixson and Cauwenberg, THIS JOURNAL, 52, 2118 (1930).

[3] Hixson and McKee, J. *Ind. Eng. Chem.*, 10,982 (1918).

[4] Phillips, THIS JOURNAL, 46,686 (1924).

[5] Flesch, Ber., 6, 478 (1873).

[6] Roderburg, *ibid.*, 6, 669 (1873).

[7] Adams and Marvel, "Organic Syntheses," John Wiley and Sons, New York, 1921, Vol. I, p. 71.

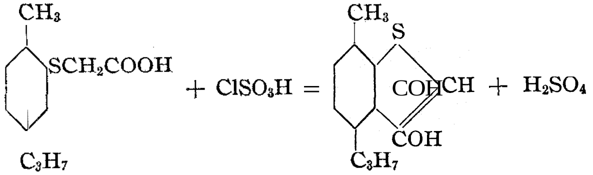
heating) and refluxed for seven hours. The thiocarvacrol was distilled from the reaction mixture with steam and dried over calcium chloride. It was purified by distillation and the fraction boiling at 235–237° was separated. The yield was 49% of the theoretical.

Anal. Calcd. for $C_{10}H_{14}S$: S, 19.27. Found: S, 19.19.

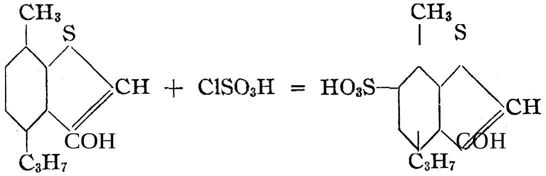
Cymene-2-thioglycolic Acid.—Thiocarvacrol (11 g.) was dissolved in 250 cc. of water containing 20 cc. of a 40% caustic soda solution. After adding a trace of sodium hyposulfite to prevent oxidation, 9 g. of chloro-acetic acid as the sodium salt in 50 cc. of water was added. The solution was heated to 70° and held for thirty minutes. The thioglycolic acid was precipitated by acidifying with hydrochloric acid at 20°. The acid was recrystallized from aqueous alcohol with a yield of 13 *g*. or 88% of the theoretical. It melted at 97°.

Anal. Calcd. for $C_{12}H_{14}OS$: S, 14.38. Found: S, 14.26.

7-Methyl-4-isopropyl-3-hydroxythionaphthene—The action of chlorosulfonic acid on cymene-2-thioglycolic acid may be represented by the reactions



(1)



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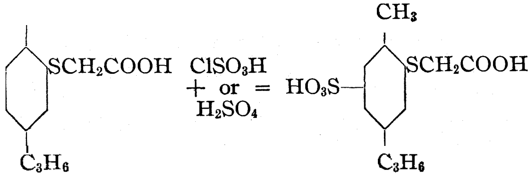

(3)

Reactions 1 and 3 may be considered as consecutive with respect to the liberated sulfuric acid or side by side with respect to the thioglycolic acid. Reaction 2, the sulfonation of the thionaphthene, is consecutive.

A series of experiments was run and the time and yields are given in Table I. The method employed was as follows. Three grams of thioglycolic acid was added in two minutes to 30 g. of chlorosulfonic acid at 0°. The reaction mass was stirred for the time given in the table and poured onto 200 g. of ice. The thionaphthene was obtained as pale yellow plates by steam distillation of the dilution mass. It was purified by redistillation with steam; melting point, 86°.

Anal. Calcd. for $C_{12}H_{14}OS$: S, 15.52. Found: S, 15.41.

Assuming that 72% of the thioglycolic acid is available for conversion to thionaphthene and that this conversion and subsequent sulfonation of the thionaphthene appear as first-order reactions due to the large excess of chlorosulfonic acid (10.3 moles per mole of thioglycolic acid), the velocity constants ratio

$$\frac{K_1}{K_2} = \frac{\text{Rate of formation of thionaphthene}}{\text{Rate of sulfonation of thionaphthene}} = 53.3$$

gave the following results when substituted in the general equation for two consecutive first-order reactions.

$$\text{Yield of thionaphthene at time } \Theta = \frac{C_0K_1}{K_1 - K_2}\, e^{-K_2\Theta}$$

where C_0 is 0.72, K_1 is 64, 8 is time in hours and K_2 is 1.2.

TABLE I

EXPERIMENTAL AND CALCULATED RESULTS

Time in minutes	60	30	7
Experimental yield, g.	27.8	41.5	61.0
Calculated yield, g.	22.0	40.5	63.8

The time at which the yield of thionaphthene is a maximum is given by: $8 = I/(K_1 - K_2)$ In $(K_1/K_2) = 0.063$ or **3.8** minutes.

The maximum yield of thionaphthene is given by

$$\text{Thionaphthene}_{(\text{max.})} = C_0 \left[\frac{K_1}{K_2}\right]^{\frac{K_2}{K_2 - K_1}} = 0.667 \text{ or } 66.7\%$$

Dyes from 7-Methyl-4-isopropyl-3-hydroxythionaphthene

7,7-Dimethyl-4,4-di-isopropyl-2,2-bis-thionaphthene Indigo. **1.**—A solution of 5 g. of thionaphthene in 100 cc. of 5% caustic soda solution was heated to SO°; 2.5 g. of sulfur was added and the heating continued until the dye was completely precipitated. The product was separated by filtration and boiled with 5% caustic soda solution to remove any excess sulfur. The yield was quantitative. It was purified by recrystallization from xylene, from which it separated as fine, dark red crystals.

Anal. Calcd. for $C_{24}H_{24}O_2S_2$: S, 15.70. Found: S, 15.77.

7-Methyl-4-isopropyl-2-thionaphthene-3-idol Indigo. **2.**—Thionaphthene (1.5 g.) and isatin (1 g.) were dissolved in 30 cc. of acetic acid and heated to 90°. Two drops of hydrochloric acid was added and the reaction held at 90° for thirty minutes. The dye was filtered, washed with alcohol and recrystallized from xylene. The yield was 1.9 g. or 79% of the theoretical.

Anal. Calcd. for $C_{20}H_{17}NO_2S$: S, 9.55. Found: S, 9.62.

7-Methyl-4-isopropyl-2-thionaphthene-2-id Indigo. 3.—Isatin chloride formed by adding 1.9 g. of phosphorus pentachloride to 1.35 g. of isatin in 50 cc. of benzene was added to a solution of 1.5 g. of thionaphthene in 200 cc. of benzene at 50°. The benzene was removed with steam and the dye after drying was recrystallized from xylene. The yield was 1.7 g. or 71% of the theoretical.

Anal. Calcd. for $C_{20}H_{17}NO_2S$: S, 9.55. Found: S, 9.63.

7-Methyl-4-isopropyl-2-thionaphthene-acenaphthene Indigo. 4.—This dye was prepared from 0.8 g. of thionaphthene and 0.7 g. of acenaphthenequinone in acetic acid containing two drops of hydrochloric acid at 90°. The product was filtered, washed with alcohol and recrystallized from xylene. The yield was 1.2 *g.* or 86% of the theoretical.

Anal. Calcd. for $C_{24}H_{18}O_2S$: S, 8.91. Found: S, 8.79.

Thioindigo Dye from Crude Cymene Sulfonate

The production of a thioindigo dye from crude cymene sulfonate was investigated. The intermediates were not purified and the thionaphthene process was modified so as to obtain the maximum yield of dye and to eliminate unnecessary mechanical operations.

Thiocarvacrol was obtained with a yield of 50.8%, which gave a yield of 99.6% of crude thioglycolic acid.

Since the thionaphthene was precipitated by dilution of the reaction mass, it was thought advisable to separate it by filtration and to oxidize it directly. The temperature of the reaction was lowered to −10° and a series of runs was made varying the time.

TABLE II

VARIATION OF YIELD OF DYE WITH TIME

Time in minutes	15	7	4
Percentage yield	26.5	55.0	58 5

A semi-technical batch gave a yield of 51.2% in large-scale equipment.

Properties of Dyes

Solubility.—These dyes are insoluble in water, dilute acids and alkalies and salts with the exception of alkaline hyposulfite.

Fastness.—The relative fastness to light was determined by exposing them for seventy-two hours to an ultraviolet lamp (used less than 200 hours) at a distance of eighteen inches. The fastness to washing was determined by applying the standard test for ninety minutes.

TABLE III

PROPERTIES OF DYES

No. of dye[a]	Color in H_2SO_4	Color of vat	Color in xylene[b]	Wash test	Fastness to light	Color of crystals
FF	Green	Yellow	Pink y	Exc.	Exc.	Red
1	Green	Yellow	Red y	Fair	Exc.	Red
BB	Green	Pale pink	Red y	Fair	Fair	....
2	R violet	Yellow	Pink	Fair	Fair	Red
3	B green	Yellow	Violet	Good	Fair	B black
4	Green	Violet	Yellow y	Good	Fair	Orange

[a] F F is the commercial dye made from o-toluidine. BB is the semi-technical hatch.

[b] y after color in'xylene denotes yellow fluorescence; exc. for excellent.

Spectrum Analyses

The spectrum analyses were made with a Koenig–Martens spectrophotometer using xylene as the solvent.

TABLE IV

SPECTRUM ANALYSES OF DYES

No. of dye	1	BB	2			3		4		
Wave length, millimicrons	559	555	510	520	529	546	575	500	510	521

The authors acknowledge their indebtedness to Dr. B. Kurrelmeyer, Department of Physics, Columbia University, for his helpful suggestions during the spectrum analyses of these dyes.

Summary

1. 7-Methyl-4-isopropyl-3-hydroxythionaphthene was prepared from sodium cymene sulfonate.

2. Four new thioindigoid dyes containing an isopropyl group were prepared.

3. The production of a thioindigo dye from crude sodium cymene sulfonate on a semi-technical scale was made.

4. Fastness tests and spectrum analyses of the dyes were made.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE ISOLATION AND IDENTIFICATION OF d-MANNURONIC ACID LACTONE FROM THE MACROCYSTIS PYRIFERA

BY WILLIAM L. NELSON AND LEONARD H. CRETCHER

RECEIVED FEBRUARY 10, 1930 PUBLISHED MAY 8, 1930

That alginic acid is a polymer of one or more aldehyde sugar acids was demonstrated by the authors in a previous communication.[1] It was shown at the same time that it is composed, at least in part, of *d*-mannuronic acid. The identity of this uronic acid was established on the basis of the fact that on oxidation it formed a dibasic acid whose diamide and diphenylhydrazide corresponded in properties to the analogous compounds prepared from pure d-mannosaccharic dilactone.

At the time of our earlier paper we had not succeeded in obtaining the aldehyde acid in crystalline condition and were consequently unable to publish any data on the physical properties of the new compound. The present paper describes experiments which led to the preparation of crystalline d-mannuronic lactone and the determination of its melting point and optical rotation.

The extraction of alginic acid from the fronds of the Macrocystis, as well as the method of hydrolysis and subsequent preparation of the barium and cinchonine salts of the hydrolysis product, has been previously described.[1] The yield of pure cinchonine salt was much less than the calculated amount based on the weight of the barium salt from which it was prepared. The mannosaccharic acid formed, in poor yield, after oxidation of the barium salt might, therefore, not have been an oxidation product of the acid whose cinchonine salt we had in hand. In other words, it remained to be proved that the cinchonine salt was that of d-mannuronic acid. This is shown to be the case in the present paper. The problem as to whether or not there are other uronic acids present in the algin remains for the future.

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[1] Nelson and Cretcher, THIS JOURNAL, 51, 1914 (1929).

Experimental Part

Preparation **of** the Lactone.—Five grams of cinchonine salt was dissolved in 125 cc. of water. The cinchonine was precipitated by addition of the calculated amount of (thrice recrystallized) barium hydroxide solution. **A** drop of phenolphthalein was added to the filtered solution and the pink color discharged by a few drops of dilute sulfuric acid. The solution was filtered through "Nuchar" and evaporated under reduced pressure to a few cc. The barium salt was then precipitated by the addition of **95%** alcohol. The salt was dissolved in water, evaporated to a small volume and again precipitated with alcohol. Barium was removed with sulfuric acid. The solution, after filtering through "Nuchar," was again evaporated under reduced pressure to a thick sirup which was placed in a vacuum desiccator for nineteen days over phosphorus pentoxide. During the drying period the material slowly crystallized. It was extracted twice with 5-cc. portions of hot glacial acetic acid and filtered. There was a considerable residue insoluble in acetic acid which proved to be inorganic. Crystallization of the lactone occurred as soon as the solution was cool. After standing for several hours, the mother liquor was decanted and the crystals were washed twice with absolute alcohol and ether. The melting point was 136–138°. After twice recrystallizing from glacial acetic acid, the melting point was constant at **140–141°**. On further heating effervescence took place at 153–155°.

Anal. Calcd. for $C_6H_8O_6$: C, **40.90;** H, **4.58.** Found: C, **40.73, 41.04; H, 4.64,** 4.59 (micro). **5.109 mg.** required **2.35** cc. of **0.01263** *N* NaOH. Calcd. neutralization equivalent: **176.** Found: **172. 0.0551** g. in **3.017** cc. of aqueous solution gave α $+$**1.64**" in a I-dm. tube; $[\alpha]_D^{25}$ **+89** 8°. There was no mutarotation in forty-six hours. Uronic acid CO_2: **0.1829** g. of sample gave **0.0462** g. of CO_2. Calcd. for $C_6H_8O_6$: CO_2, **25.0.** Found: CO_2, **25.26.**

The lactone was titrated for aldehyde according to the method of Willstätter and Schudel.[2] **A** large excess of iodine over the amount theoretically required for an aldehyde of molecular weight **176** was required. Much of the iodine was consumed in the production of iodoform. This is in harmony with our observation that mannosaccharic acid was easily oxidized by cold alkaline iodine with formation of much iodoform. The study of this reaction and the identification of its products are now under way.

Identification **of** the **Lactone.**—0.250 g. of lactone and **0.924** g. of barium benzoate[3] were dissolved in **30** cc. of water; **0.1** cc. of bromine was added and the solution allowed to stand in the dark for forty-eight hours. The solution was filtered to remove the precipitated benzoic acid and the excess bromine was evaporated by passage of a stream of air. The solution was twice extracted with chloroform and heated for thirty minutes with an excess of barium carbonate. After filtering, the solution was evaporated to a few cc. under reduced pressure. **A** granular precipitate of the barium salt formed during evaporation. The precipitation was completed by the addition of several volumes of alcohol. The salt was dissolved in hot water and again evaporated and treated with alcohol. After filtering and washing with alcohol, the barium was removed with sulfuric acid, the solution filtered through decolorizing carbon and evaporated, in *vacuo,* to a sirup. Crystallization was induced by seeding with a crystal of mannosaccharic lactone. The partially crystalline sirup was dried for twenty-four hours in a vacuum desiccator over phosphorus pentoxide. The material was twice extracted with about 5-cc. portions of hot glacial acetic acid and filtered. On cooling the product separated in crystalline condition. Again filtered, washed with alcohol and ether and dried, the compound melted at 182–184° with decomposition.

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[2] Willstatter and Schudel, *Ber.*, 51, 780 **(1918).**

[3] Hudson and Isbell, THIS JOURNAL, 51, **2225 (1929).**

A sample of pure mannosaccharic lactone melted at 182–183° when heated at the same rate and there was no change in the mixed melting point.

Optical rotation.—0.0360 g. in 3.017 cc. of aqueous solution rotated +2.38° in a 1-dm. tube: $[\alpha]_D^{20}$ +199.5°. The sample of d-mannosaccharic dilactone prepared in this Laboratory had $[\alpha]_D^{23}$ +199.8°. Titration with alkali: 0.0102 g. required 2.01 cc. of 0.0590 N NaOH. Neutralization equivalent, calcd.: 87. Found: 86.

The **Diamide.**—The solution which had been used for determination of the optical activity was evaporated to dryness under reduced pressure and several drops of concd. ammonium hydroxide was added. After several hours a white crystalline compound was deposited. It melted at 189° and after mixing with pure d-mannosaccharic diamide the melting point was unchanged.

Summary

A hitherto unknown aldehyde sugar acid—d-mannuronic—has been isolated, in the form of its lactone, from the hydrolysis product of the algin in the *Macrocystis pyrifera.*

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION NO. 189 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

THE NITRATION OF ABIETIC ACID AND THE STUDY OF SOME OF ITS NITROGEN DERIVATIVES[1]

BY L. A. GOLDBLATT WITH ALEXANDER LOWY AND W. B. BURNETT

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A number of investigators have studied the effect of nitric acid, nitrous acid and nitrogen oxides on more or less purified mixtures of rosin acids. Easterfield[2] reported that nitro derivatives are obtained when abietic acid is treated with nitric acid in glacial acetic acid solution, but gave no experimental data. Johansson[3] first reported a crystalline nitro derivative of abietic acid. This was obtained in 15% yield by the action of fuming nitric acid at a low temperature on an abietic acid of m. p. 155–168° and $[\alpha]_D$ −28.6°. This, a dinitro compound, $C_{20}H_{28}N_2O_6$, m. p. 178–184° and $[\alpha]_D$ +44.25°, was sensitive to light and was easily esterified. Aschan and Virtanen[4] duplicated the work of Johansson on pinabietic acid and obtained the same product. They concluded that Johansson's abietic acid was in reality pinabietic acid.

Dubourg[5] also attempted, unsuccessfully, to duplicate the work of Johansson on an abietic acid $[\alpha]_D$ −100°. Dubourg, however, succeeded

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[1] This paper is an abstract of a thesis presented to the Graduate School of the University of Pittsburgh by L. A. Goldblatt in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] T. H. Easterfield and George Bagley, J. *Chem. Soc.*, 85, 1238 (1904).

[3] M. D. Johansson, *Arkiv. Kemi. Min. Geol.*, **6**, No. 19, July (1917), and *Mon. sci.*, 88, 73 (1921).

[4] Ossian Aschan and A. I. Virtanen, *Ann.*, 424, 150 (1921).

[5] J. Dubourg (a) *Bull. inst. pin.*, No. 41, 241 (1927), and (b) No. 59, 138 (1929).

in isolating several white crystalline nitro derivatives of abietic acid. A dinitro derivative, $C_{19}H_{26}N_2O_6$, m. p. 162–165° and $[\alpha]_D$ $-115°$, was obtained by the action of concentrated nitric acid on a hot alcohol or acetic acid solution of abietic acid. The maximum yield was 33%. This compound was stable toward light and air, markedly levorotatory and could be esterified only with difficulty. It was, therefore, different from the dinitro compound of Johansson and Aschan and Virtanen. A trinitro compound, $C_{16}H_{17}N_3O_8$, m. p. 156–158° and $[\alpha]_D$ $-136.2°$, was prepared by the action of fuming nitric acid on the dinitro derivative. A different trinitro derivative, $C_{20}H_{23}N_3O_8$, m. p. 177–178° and $[\alpha]_D$ $-95°$, was prepared with a yield of **2–3%** by the action of concentrated nitric acid at room temperature on a solution of abietic acid in carbon tetrachloride.

Patents covering the products obtained by the action of nitric acid on rosin or rosin acids have been granted to Fry, Kesler and Arnot,[6] but these patents were entirely concerned with empirical processes.

There has been considerable controversy as to the products obtained by previous investigators from the nitration of abietic acid. Further, only low yields of products were reported and practically nothing was said as to the fate of the remainder of the abietic acid used. It was therefore deemed desirable to make a further study of the nitration of abietic acid. It was also the purpose of this investigation to study certain chemical properties of abietic acid and derivatives such as salts and esters with special reference to nitration and the reduction of nitro bodies produced.

Experimental Part

Nitration of Abietic Acid.—Twenty-four experiments were conducted to observe the effect of nitric acid on abietic acid or sodium tetra-abietate, prepared according to the method of Kesler,[7] dissolved in alcohol. The effects of concentration of abietic acid, concentration of nitric acid, stirring, temperature and time of reaction were studied. In general, two products were obtained, a white crystalline dinitro derivative and a yellow uncrystallizable nitrogen-containing product. The formation of the white dinitro compound was accompanied by a vigorous effervescence and frothing and, in general, was favored by a high temperature, a short time of reaction and an excess of nitric acid. A maximum yield of 40% of the white dinitro compound was obtained in this series of experiments. A yield of 50% was obtained in an experiment in which the combined mother liquor and wash alcohol from one nitration was used as the solvent for a second nitration.

A **Typical** Experiment.—One hundred grams of abietic acid, m. p. 166° and $[\alpha]_D^{20}$ $-67°$, and **200** cc. of 95% ethyl alcohol were placed in a 5-liter round-bottomed pyrex flask. The mixture was heated to boiling on a water-bath. When solution was effected,

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[6] George Fry, U. S. **754,298,** March **8, 1904;** J. J. Kesler, U. S. **922,596, May 25, 1909;** Robert Arnot, German Patent **337,954,** June 7, **1921;** French Patent **520,984,** July 5, **1921.**

[7] C. C. Kesler, Alexander Lowy and W. F. Faragher, THIS JOURNAL, 49, **2898** **(1927).**

fifteen 5-cc. portions of nitric acid (sp. gr. 1.42) were added at half-minute intervals. The last 5 cc. was added in 0.5-cc. portions at half-minute intervals, and was allowed to run down the side of the flask. This procedure is necessary in order to start a localized reaction. The solution was colored a deep brownish-black at this stage. A violent frothing accompanied by the evolution of a small amount of nitrogen oxides, carbon dioxide and acetaldehyde commenced when the last portion was added. The flask was quickly removed from the water-bath and the upper surface cooled by means of cold wet cloths to prevent expulsion of the liquid by the violent frothing. The reaction soon subsided and a clear orange colored liquid resulted.

On cooling, needle-like crystals gradually formed throughout the entire liquid. The crystals were filtered by suction and washed with 150 cc. of alcohol. They were recrystallized from alcohol and dried in vacuo over anhydrous calcium chloride. Twenty g. of a white crystalline material, discussed as the white dinitro compound, m. p. 170–171° and $[\alpha]_D^{20}$ −118°, was thus obtained. (All melting points have been corrected. The rate of heating for the last 20° was 2–3° per minute. The rotation in this case was measured on a 0.6% solution in 95% ethyl alcohol.) The combined filtrate and wash liquor was placed in an ice-box overnight. The additional crystalline deposit was filtered and treated like the above-described first crop. In this way an additional 10 g. of the white crystals was obtained. In order to get a second crop, this cooling should not be too intense as an orange oily product separates when this solution is cooled to −10°.

The orange colored filtrate was then poured with vigorous stirring into 3 liters of water acidulated with 100 cc. of concentrated hydrochloric acid. An orange-yellow amorphous precipitate was thus obtained; (when the water was not previously acidulated a gelatinous precipitate, difficult to filter, was formed). This product was filtered by suction and washed free of chlorides with about 10 liters of water. When dried in *vacuo* over calcium chloride, 75 g. of a yellow nitrogen-containing product (discussed as the yellow nitrogen-containing product) was obtained.

Neither the white dinitro compound nor the yellow product were obtained when an alcoholic solution of abietic acid was treated with ethyl nitrate, used alone or with a little nitric acid, as the nitrating agent.

Other Nitration Experiments.—Seventeen experiments were conducted to observe the effect of various amounts of nitric acid on abietic acid in acetic acid solution at temperatures ranging from 25–120°. Very little reaction took place at low temperatures and there was no frothing below 90°. Above 90° frothing occurred, the reaction mixture became orange-red in color and the yellow nitrogen-containing product was obtained. When acetic acid was used as a solvent, only a small quantity of the white crystalline dinitro acid was obtained. The maximum yield of this compound, 4%, was obtained in an experiment in which 4 cc. of concentrated nitric acid was added in 0.5-cc. portions at half-minute intervals to a solution of 10 g. of abietic acid in 25 cc. of acetic acid at a temperature of 90°.

Several experiments were carried out on the nitration of abietic acid dissolved in benzene, nitrobenzene, carbon tetrachloride and 1,4-dioxan. The white dinitro compound was not obtained in any of these experiments. The use of concentrated nitric acid and elevated temperature resulted in the formation of the yellow nitrogen-containing product.

A number of experiments were conducted in which abietic acid or sodium tetra-abietate was treated directly with nitric acid. Oxidation occurred and no crystalline nitro derivatives of abietic acid were isolated. The results obtained were invariably the yellow uncrystallizable nitrogen-containing material.

The White Dinitro Compound.—The rate of heating affects the melting point of this compound. After two recrystallizations from alcohol, the following melting points were observed. Rate of heating above 140°: 1° per minute, m. p. 163.8–164.2°; 1.5° per minute, m. p. 165.9–166.2°; 2 5° per minute, m. p. 171.2–171.4°. Successive recrystallizations from alcohol, ether, acetic acid and acetone did not appreciably alter the melting points taken at corresponding rates.

The analytical data presented by Dubourg[5a] are quite inconclusive. Since the melting point was higher and since Dubourg reported the loss of a methyl group, this compound was analyzed. Analysis substantiated the formula $C_{19}H_{26}N_2O_6$ proposed by Dubourg.

Anal. Calcd. for $C_{19}H_{26}N_2O_6$ (without CH_3): C, 60 28; H, 6 93; N, 7 41, neutral equivalent, 378.2. Calcd. for $C_{20}H_{28}N_2O_6$ (with CH_3): C, 61.19; H, 7.19; N, 7.16; neutral equivalent, 392.2. Found: C, 59.94, 59.45; H, 7 30, 7.21; N, 7.57, 7.69, 7.33, 7.63, 7.67; neutral equivalent, 374.5, 367.4, 373.7.

The sodium salt was precipitated by adding an excess of 30% aqueous sodium hydroxide to an alcoholic solution of the dinitro compound. After washing with alcohol and drying in vacuo over calcium chloride, it was analyzed as the sulfate.

Anal. Calcd. for $C_{19}H_{25}N_2O_6Na$ (without CH_3): Na, 5.75. Calcd. for $C_{20}H_{27}N_2O_6$-Na (with CH_3): Na, 5.56. Found: Na, 5.56, 5.78, 5.71.

The ethyl ester, m. p. 157.5–157.8°, was prepared by refluxing an alcoholic suspension of the sodium salt with diethyl sulfate. This compound was also prepared by the action of nitric acid on an alcoholic solution of ethyl abietate,[8] b. p. 195–ZOO° (4 mm.).

It is quite difficult to saponify this ester. Analysis indicated the formula $C_{21}H_{30}N_2O_6$ for this compound and thus further substantiated the formula $C_{19}H_{26}N_2O_6$ for the free acid.

Anal. Calcd. for $C_{21}H_{30}N_2O_6$ (without CH_3): C, 62.04; H, 7.44; N, 6.90. Calcd. for $C_{22}H_{32}N_2O_6$ (with CH_3): C, 62.82; H, 7.67; N, 6.65. Found: C, 61.74, 61.63; H, 7.52, 7.61; N, 7.21, 7.04, 7.17, 7.13, 7.12.

Molecular weight determinations of the white dinitro compound indicate slight association in ethyl acetate solution and considerable association in benzene solution. Calcd. for $C_{19}H_{26}N_2O_6$ (without CH_3): mol. wt., 378.2. Calcd. for $C_{20}H_{28}N_2O_6$ (with CH_3): mol. wt., 392.2. Found: mol. wt., 401.1 (in ethyl acetate); 571.2 (in benzene).

Saponification experiments indicated that the white dinitro compound is a nitro derivative of abietic acid and not a nitrate. It was reduced by means of zinc dust and acetic acid, zinc dust and hydrochloric acid in 50% ethyl alcohol and alkaline sodium "hydrosulfite," $Na_2S_2O_4$. It was also reduced catalytically in ethyl acetate solution with a platinum oxide catalyst, $PtO_2 \cdot H_2O$, prepared according to the method of Adams and Shriner.[9]

Nitrogen oxides were evolved during the reduction in acid solution. Ammonia was evolved during the reduction in alkaline solution. A white solid melting at 171.5–172" was precipitated in 80% yield from the ethyl acetate solution during the catalytic reduction. One mole of the white dinitro compound absorbed 1.74 moles of hydrogen during the reduction. The reduction product evolved ammonia when dissolved in hot alcohol or when treated with cold dilute aqueous alkali.

The Yellow Nitrogen-Containing Product.—The yellow nitrogen-containing product did not have a definite melting point but decomposed above 100°. A 0.5% solution in alcohol gave $[\alpha]^{20}_{D}$ −36°. This product was only slightly soluble in chloroform, carbon tetrachloride and petroleum ether. Attempts to separate components of this material

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[8] Supplied by the Hercules Powder Company.

[9] Roger Adams and R. I,. Shriner, THIS JOURNAL, 45, 2171 (1923).

and to secure crystalline products by the use of a number of solvents, mixtures of solvents and partial precipitation of metallic salts were unsuccessful. This product dissolved in cold aqueous sodium hydroxide, potassium hydroxide and ammonium hydroxide, imparting a deep red color to the solution. Abietic acid dissolved in these reagents forming colorless solutions. The respective products were reprecipitated by bubbling carbon dioxide through the solution. The analytical data show this to be a nitrogen-containing hydroxylated acid.

Anal. Found: C, 63.76, 63.60, 63.27, H, 7.83; N, 6.74, 6.46, 6.70. Neutral equivalent, 365.5, 367.7. Acetyl chloride indicated the presence of 0.84 OH per neutral equivalent.

The red alkaline aqueous solution of this yellow nitrogen-containing product completely absorbed oxygen from air; 300 cc. of a 3% alkaline solution absorbed 20 cc of oxygen in fifteen minutes; 1.8 g. dissolved in 100 cc. of 1% aqueous sodium hydroxide absorbed 92 cc. of oxygen in the course of three days. The alkaline solution froths or lathers quite readily.

The yellow product was reduced in the same manner as the white dinitro compound. Nitrogen oxides were evolved during reduction in acid media and ammonia was evolved during reduction in alkaline media. The evolution of ammonia when the catalytic reduction product was made alkaline indicated the reduction of a nitro group. No crystalline reduction products of the yellow nitrogen-containing material could be obtained. Analysis of the brown solid obtained by pouring the zinc–acetic acid reduction product into water further indicated the loss of nitrogen from this product during the reduction.

Anal. Found: (before reduction): N, 6.74, 6.46; (after reduction): N, 3.54, 3.64.

A light yellow sodium salt was precipitated from acetone solution when aqueous sodium hydroxide was added drop by drop. Attempts at esterification of the sodium salt of the yellow product with dimethyl or diethyl sulfate resulted only in uncrystallizable tars.

Summary

1. A study of the conditions of nitration of abietic acid and some of its derivatives has been made.

2. Two main products were obtained: a white crystalline dinitro acid, $C_{19}H_{26}N_2O_6$ (substantiating Dubourg's results), m. p. 171.2–171.4° (Dubourg reported a m. p. of 162–165°) and a yellow amorphous nitrogen-containing product, decomposing above 100°. The latter is a hydroxylated nitro derivative of abietic acid while the former is not. The properties of these products have been studied.

3. The alkaline solution of the yellow nitrogen-containing product readily absorbs oxygen.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE REACTION BETWEEN THIOCARBANILIDE AND MONOCHLORO-ACETIC ACID IN ALCOHOL AND IN ACETIC ACID SOLUTION[1,2]

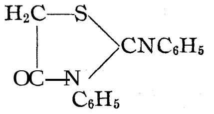
BY KLARE S. MARKLEY AND E. EMMET REID

RECEIVED FEBRUARY 17, 1930 PUBLISHED MAY 8, 1930

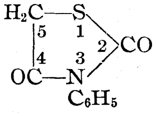
Following the general directions of Lange[3] for the preparation of diphenylisothiohydantoin from thiocarbanilide and monochloro-acetic acid, in order to study its condensation with aldehydes, Hann and Markley[4] and later Kingsbury and Markley[5] observed that the reaction conditions markedly affected not only the yield but also the compound which was formed. No explanation of these observations could be obtained from the papers of Lange, Andreasch,[6] Liebermann and Lange,[7] and Liebermann,[8] who previously prepared diphenylisothiohydantoin for the purpose of studying its constitution, since these authors failed to mention either the yields obtained or the effect of variations in the experimental conditions on the reaction. A number of experiments were therefore undertaken to determine what influence the concentration of reactants, time of reflux, solvent and catalyst had on the course of the reaction.

Results and Discussions.—As a result of this investigation it has been determined that, irrespective of solvent, the primary reaction between thiocarbanilide and monochloro-acetic acid is the formation of diphenylisothiohydantoin (I). From the results recorded in Table I it is evident that with alcohol as solvent the best yields are obtained with a short period of reflux, a small ratio of solvent to reactants, a slight excess of monochloro-acetic acid and the addition of sufficient anhydrous sodium acetate to remove the hydrochloric acid from the reaction as rapidly as it is formed. A high yield of diphenylisothiohydantoin may likewise

I



II



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[1] Presented in abstract before the Organic Division at the Columbus meeting of the American Chemical Society, April, 1929.

[2] From a part of the Ph.D. dissertation of Klare S. Markley, June, 1929. Parts II and III to follow.

[3] Lange, *Ber.*, 12, 595 (1879).

[4] Hann and Markley, *J. Washington Acad. Sci.*, 16, 169 (1926).

[5] Kingsbury and Markley, *ibid.*, 18, 558 (1928).

[6] Andreasch, *Ber.*, 12, 1385 (1879).

[7] Liebermann and Lange, *ibid.*, 12, 1588 (1879).

[8] Liebermann, *Ann.*, 207, 121 (1881).

be obtained with glacial acetic acid as solvent provided precautions are taken to remove the hydrogen chloride formed in the primary reaction.

TABLE I

EFFECT OF REACTION CONDITIONS UPON THE YIELD OF DIPHENYLISOTHIOHYDANTOIN

No.	$(C_6H_5NH)_2CS$, g.	$CH_2ClCOOH$, g.	Solvent used Kind	Solvent used cc.	Other reagents used Kind	Other reagents used Amount	Time of reflux, hours	Crude diphenylisothiohydantoin g.[a]	Crude diphenylisothiohydantoin %	% N[b]
1	25	10.5	95% alc.	400	......	...	4.5	10.8	36.8	10.38
2	25	12.0	95% alc.	400	......	...	4.5	11.6	39.5	10.42
3	50	25.0	95% alc.	400	......	...	2.5	25.0	42.5	10.26
4	25	12.0	95% alc.	300	......	...	2.5	13.0	44.2	10.74
5	25	12.0	95% alc.	300	......	...	2.0	13.0	44.2	10.28
6	100	45.0	95% alc.	400	......	...	1.25	54.0	45.9	10.38
7	100	50.0	95% alc.	500	......	...	1.25	58.0	49.3	...
8	25	12.0	100% alc.	200	......	...	2.5	13.0	44.2	10.27
9	50	25.0	100% alc.	300	CH_3COONa	10 g.	3.5	45.0[c]	76.6	...
10	50	25.0	CH_3COOH	60	......	...	5.5	..	..	..
11	25	12.0	CH_3COOH	75	CH_3COONa	10 g.	2.0	24.0[c]	81.7	10.38
12	25	12.0	95% alc.	500	HCl	10 cc.	5.5	..	..	...

[a] The actual yields are somewhat higher due to the slight solubility of the compound in 95% alcohol. [b] Theoretical nitrogen: 10.45%. [c] Reaction mixture treated with water to separate the CH_3COONa.

When these precautions are not observed a mixture of diphenylisothiohydantoin and 3-phenyl-2,4-thiazolidione[9] (II) is formed in alcohol solution, whereas with glacial acetic acid (in proper proportion)[10] as the solvent and provided the time of reflux is sufficiently prolonged (five hours or more), practically quantitative yields of the latter compound are obtained, as indicated in Table II. It is apparent that the cyclic diketone results from the secondary hydrolysis of the diphenylisothiohydantoin under the influence of the hydrochloric acid formed in the primary reaction, as was suggested by Lange.

The hydrolysis of diphenylisothiohydantoin to form 3-phenyl-2,4-thiazolidione, however, is not the only factor which lowers the yield of diphenylisothiohydantoin as prepared in alcoholic solution, since the mother liquors from these preparations were found to contain, in addition to 3-phenyl-2,4-thiazolidione, urea, phenyl mustard oil and phenylthiourethan. The addition of hydrochloric acid to the original reaction mixture (Expt.

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[9] Liebermann and Völtzkow, *Ber.*, 13, 276 (1880), obtained the same compound by heating phenylthiourethan, monochloro-acetic acid and absolute alcohol under pressure; P. Meyer, *Ber.*, 14, 1659 (1881), by the hydrolysis of o-phenylthiohydantoic acid and o-phenylthiohydantoin; Evers, *ibid.*, 21, 962 (1888), by the reaction of ethyl-, propyl- and allylphenyldithiourethan and monochloro-aceticacid; Wheeler and Barnes, Am. *Chem. J.*, 24, 60 (1900), by melting together phenylthiourethan and monochloroacetic acid.

[10] If the volume of glacial acetic acid is too large, diphenylisothiohydantoin is not completely converted into the cyclic diketone; if too small, partial decomposition ensues with the formation of phenyl mustard oil.

TABLE II

EFFECT OF REACTION CONDITIONS UPON THE YIELD OF 3-PHENYL-2,4-THIAZOLIDIONE

No	$(C_6H_5NH)_2CS$, g.	$CH_2ClCOOH$, g.	CH_3COOH, cc.	Time of reflux, hours	Yield of crude diketone g.	Yield of crude diketone %	Solvent used for final crystallization	Purified compound, % N[a]
1	50	25	75	2.5	43"	..	.....	..
2	25	12	25	2.0	16[c]	..	......	..
3	50	25	100	4.25	27[d]	..	......	..
4	25	12	40	4.0	18"	..	......	..
5	25	12	25	4 25	14	66.2	Not recryst.	7.27
6	50	25	65	4.5	36	85.1	CH_3COOH	7.35
7	25	12	25	4.0	18.3	86.5	CH_3COOH	7.23
8A	50	25	60	5.5	40	94.3	95% alc.	7.27[f]
8B	50	25	60	5.5	39	92.2	CH_3COOH	
9	25	12	30[g]	3.0	14	66.2	Not recryst.	7.28

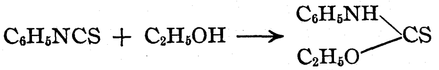
[a] Theoretical nitrogen, 7.25%. [b] 17.0 g. of diphenylisothiohydantoin separated from crude product. [c] 4.5 g. of diphenylisothiohydantoin isolated from crude product. [d] Analysis of crude compound gave 8.53% N; impurity found to be diphenylisothiohydantoin. [e] Nitrogen of crude product, 8.83%. Diphenylisothiohydantoin isolated from mixture. [f] After drying at 133°. [g] 10 cc. of concd. HCl added to reflux mixture; considerable phenyl mustard oil formed.

12, Table I) led to the formation of but small amounts of diphenylisothiohydantoin and 3-phenyl-2,4-thiazolidione and considerable quantities of phenyl mustard oil and phenylthiourethan, whereas the addition of hydrochloric acid to an alcoholic solution of diphenylisothiohydantoin led to its quantitative transformation into 3-phenyl-2,4-thiazolidione. Summarizing these results, the following reactions may be assumed to occur during the reaction of thiocarbanilide with monochloro-acetic acid in alcohol solution.

$$(C_6H_5NH)_2CS + CH_2ClCOOH \longrightarrow C_{15}H_{12}ON_2S + H_2O + HCl \qquad (I)$$

$$C_{15}H_{12}ON_2S + H_2O + HCl \longrightarrow C_9H_7O_2NS + C_6H_5NH_2 + HCl \qquad (II)$$

$$(C_6H_5NH)_2CS \longrightarrow C_6H_5NCS + C_6H_5NH_2 \qquad (III)$$



$$C_6H_5NCS + C_2H_5OH \longrightarrow \begin{matrix} C_6H_5NH \\ C_2H_5O \end{matrix}\!\!>CS \qquad (IV)$$

Experimental

Diphenylisothiohydantoin.—The general method used in preparing the diphenylisothiohydantoin was briefly as follows: 25 to 100 g. of thiocarbanilide and slightly more than the corresponding molar quantity of $CH_2ClCOOH$ were dissolved in 300 to 500 cc. of alcohol and heated under a reflux condenser for one and one-fourth to five hours. As long as the solid phase of the compound was absent, no crystals separated although the solution was enormously supersaturated with respect to diphenylisothiohydantoin. At the expiration of the time of refluxing, the hot solution was filtered with the aid of a hot water funnel. The diphenylisothiohydantoin separated from the hot filtrate in beautifully iridescent, very thin plates. When the volume of alcohol was sufficiently large the compound was found to separate in a very pure form as was shown by nitrogen analysis and melting point. When the compound was recrystallized, 3 to 5 times the volume of boiling alcohol was necessary to redissolve it as compared with the original volume of solvent from which it was obtained. Upon pouring the hot alcoholic solution into cold water, pure diphenylisothiohydantoin separated as a white microcrystalline powder and not as an oil as was reported by Lange. It did, however, separate as a red oil from the crude reaction mixture when the latter was treated with water in a similar manner A solubility determination of diphenylisothiohydantoin in 95% alcohol at 27° gave a value of 0.35 g. per 100 g. of solvent, or 0.28 g. per 100 cc. The optical properties of diphenylisothiohydantoin as determined by Mr. G. L. Keenan of the Bureau of Chemistry and Soils were as follows. Recrystallized from 95% alcohol the compound consisted of thin, colorless, micaceous plates. The indices of refraction were found to be n_α 1.654, n_β 1.690, both ±0.003, $n_\gamma > 1.734$. In convergent polarized light, crossed nicols, biaxial interference figures were observed occasionally, particularly in plates perpendicular to an optic axis.

3-Phenyl-2,4-thiazolidione.—Since the condensation of diphenylisothiohydantoin with aromatic aldehydes is readily effected in glacial acetic acid, it was thought that this acid would prove to be an ideal solvent for its preparation. Nitrogen analysis, melting point and microscopic examination of the resulting product showed, however, that the compound formed was 3-phenyl-2,4-thiazolidione and not the expected diphenylisothiohydantoin. Almost quantitative yields were obtained when the following conditions were observed: 50 g. of $(C_6H_5NH)_2CS$, 25 g. of $CH_2ClCOOH$ and 60 cc. of glacial acetic acid were shaken together in a 300-cc. flask to form a paste. Partial solution occurred, accompanied by considerable cooling. The flask was connected with a reflux condenser and gentle heat applied to effect complete solution, after which vigorous boiling was maintained for five hours or more. On cooling, the contents of the flask solidified to a mass of star-shaped clusters of yellow needles quite unlike diphenylisothiohydantoin. Following the addition of water the mass was disintegrated by shaking, and the product washed first by decantation and then on a Büchner funnel. On recrystallization from alcohol it separated in the form of bushy rosets of long thin yellow needles.

Mother Liquors of Diphenylisothiohydantoin.—When the mother liquors from the alcohol series of preparations, which always possessed a typical phenyl mustard oil odor, were evaporated either by the aid of heat or spontaneously, crystallization continued with the separation of a compound which appeared to the casual view to be diphenylisothiohydantoin. When evaporation was continued to dryness it was observed that two different layers formed; an upper one which appeared like diphenylisothiohydantoin and a lower one composed of a dark red, oily material shot through with fine needle-like crystals. When heated to 100° or to an even lower temperature the whole mass melted to a clear red oil which solidified again on cooling. Examination of the mother liquors from Prepns. 3, 5, 7 and 8 (Table I) led to the isolation and identification of the following compounds: phenyl mustard oil, phenylthiourethan, diphenylisothiohydantoin, 3-phenyl-2,4-thiazolidione and diphenylthiourea. Although quantitative separations were impracticable, it appeared that phenyl mustard oil and phenylthiourethan comprised the bulk of the products contained in the mother liquors.

In addition to the experiments recorded in Tables I and II, two additional preparations were made by refluxing for two hours 25 g. of diphenylthiourea and 12 g. of $CH_2ClCOOH$ dissolved in 300 and 250 cc. of 95% alcohol, respectively. After separating the crystallized diphenylisothiohydantoin in the usual manner, the mother liquors and washings were evaporated until but 25 to 35 cc. of a red oil remained, which on cooling solidified to a light yellow crystalline mass. To the first residue there was added 5 g. of $CH_2ClCOOH$, 5 cc. of concd. hydrochloric acid and 60 cc. of acetic acid, and to the second 25 cc. of acetic acid only. Both mixtures were then refluxed for four hours. After cooling the reaction mixtures were poured into large volumes of cold water and allowed to stand for twenty-four hours to separate the crystalline material from the oil. The crude product which separated was then collected on a Buchner funnel, washed with water, dried and weighed. In the first case diphenylisothiohydantoin and 3-phenyl-2,4-thiazolidione equivalent to 49.4 and 17.5% and in the second case 42.5 and 26%, respectively, of the original thiocarbanilide were recovered.

Secondary Formation of **3-Phenyl-2,4-thiazolidione.**—Since hydrochloric acid separated in molar proportions in the course of the reaction, its effect on diphenylisothiohydantoin and the original reactants was studied in this concentration. Two samples of 10 g. each of pure diphenylisothiohydantoin were dissolved in 60 cc. of glacial acetic acid and 1.35 g. of hydrochloric acid added in the form of its concentrated aqueous solution. To the second sample was added 6 g. of anhydrous sodium acetate. Both samples were boiled under a reflux condenser for four hours. Upon cooling, the reaction mixtures were poured into large volumes of cold water, the precipitates collected on Büchner funnels and washed to remove the acetic acid, hydrochloric acid and sodium acetate. After drying at 105°, the product from the first reaction, amounting to 7.0 g. (calcd. 7.2 g.), was identified by microscopic examination and nitrogen analysis as 3-phenyl-2,4-thiazolidione. The diphenylisothiohydantoin was quantitatively recovered in the second case.

Summary

The reaction between thiocarbanilide and monochloro-acetic acid has been studied in alcohol and in acetic acid under different experimental conditions and the probable mechanism of the reaction established. With anhydrous solvent containing sufficient anhydrous sodium acetate to remove both the water and hydrogen ions from the sphere of action, the maximum yield of diphenylisothiohydantoin is obtained. With acetic acid as solvent and a period of refluxing exceeding five hours, almost quantitative yields of 3-phenyl-2,4-thiazolidione are obtained.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE VESICANT ACTION OF CHLORO-ALKYL FURFURYL SULFIDES

BY HENRY GILMAN AND A. P. HEWLETT

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Introduction

In connection with studies concerned with furfural and its derivatives,[1] we have had occasion to synthesize β-chloro-ethyl furfuryl sulfide and γ-chloropropyl furfuryl sulfide. It was considered worth while to test these compounds for their vesicant action. This we have done. The β-chloro-ethyl sulfide has a marked vesicant action, which, however, is not so great as that of mustard gas ($(ClCH_2CH_2)_2S$). The γ-chloropropyl compound is without vesicant action. These results are in complete agreement with recent studies by Kirner.[2] He showed that in a

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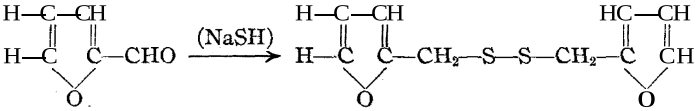
[1] See *Iowa State College J. of Science*, Vols. **2, 3, 4** (1928, 1929, 1930).

[2] Kirner, THIS JOURNAL, 50, 2446 (1928).

series of related chloro-alkyl sulfides only the β-chloro-ethyl (and not the α-chloro-methyl nor the γ-chloropropyl) sulfide had vesicant properties.

The following reactions were used for the preparation of our compounds in quite satisfactory yields.

The y-chloropropyl furfuryl sulfide when applied to the skin in undiluted form produces no skin irritation.



(I)

$$C_4H_3OCH_2SSCH_2C_4H_3O \xrightarrow{(H)} 2C_4H_3OCH_2SH \qquad \text{(II)}$$

$$C_4H_3OCH_2SH \xrightarrow{(C_2H_5MgBr)} C_4H_3OCH_2SMgBr \qquad \text{(III)}$$

$$C_4H_3OCH_2SMgBr + 2ClCH_2CH_2OSO_2C_6H_4CH_3\ (p) \longrightarrow$$
$$C_4H_3OCH_2SCH_2CH_2Cl + ClCH_2CH_2Br + (p\text{-}CH_3C_6H_4SO_2O)_2Mg \qquad \text{(IV)}$$

Experimental Part

Furfuryl Disulfide (See Reaction I).—The disulfide was prepared after recent patent directions.[3] Dry hydrogen sulfide was added rapidly over a two-hour period to a mixture (cooled by ice and salt) made up of 288 g. (3.0 moles) of furfural in 1500 cc. of 95% alcohol and 250 g. (3.2 moles) of sodium sulfide. After permitting the mixture to stand at room temperature overnight, the liquid was separated from the undissolved sodium sulfide, refluxed for one hour and then distilled from a water-bath to remove one liter of the alcohol. The residue from the water-bath distillation was poured into four liters of water and extracted with two liters of ether. The ether layer was separated, dried over sodium sulfate, and then the ether was removed by distillation from a water-bath. The residue of disulfide was thereupon reduced without further purification. However, a small portion was found to distil with some decomposition and discoloration at 160–165° (5 mm.). The boiling point previously3 given is 112–115" (0.5 mm.), and the melting point 10–10.5°.

Furfuryl Mercaptan (See Reaction II).—To the crude disulfide dissolved in 500 cc. of alcohol and 25 cc. of acetic acid was added in small portions 130 *g*. (2 atoms) of powdered zinc. The time required for the addition of zinc was about one hour, during which period the mixture was refluxed on a water-bath and stirred vigorously. Subsequent to an additional two hours of refluxing, a saturated solution of oxalic acid containing 180 g. (1.43 moles) was added, and the whole subjected to steam distillation. The distillate was extracted with ether, dried over sodium sulfate and distilled. The yield of mercaptan distilling at 155' at atmospheric pressure was 250 g. or 73%. The boiling points reported previously are 45–47° (12 mm.)[3] and 84° (65 mm.).[4] The p-nitrobenzoate of the mercaptan was found to melt at 77°, which is in agreement with that reported elsewhere.' Furfural mercaptan is a colorless liquid, very stable and with an extremely disagreeable odor.

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[3] Staudinger and Reichstein, Canadian Patent 283,765 (Oct. 2, 1928); *C.* **A.**, **22**, 4537 (1928); Internationale Nahrungs- und Genussmittel A.-G., Brit. Patent 286,152 (July 25, 1927); *C.* **A.**, **23**, 155 (1929).

[4] Kirner, THIS JOURNAL, 51, 3134 (1929), has just reported the preparation of furfuryl mercaptan in a 33% yield by hydrolysis, without isolation, of the product obtained by condensation of a-furfuryl chloride with thiourea.

β-Chloro-ethyl Furfuryl Sulfide (See Reactions III and IV).—The reactions used for the preparation of the chloro-alkyl furfuryl sulfides are applications of the alkylating action of alkyl sulfonates on organomagnesium halides reported previously from this Laboratory.[5]

An ethereal solution of ethylmagnesium bromide prepared from 24 g. (2.2 moles) of ethyl bromide in 250 cc. of ether was siphoned from unaltered magnesium into a one-liter, three-necked flask provided with a mercury-sealed mechanical stirrer, condenser and separatory funnel. To the Grignard solution, cooled by an ice–salt mixture, was added dropwise a solution of 22.8 g. (0.2 mole) of the furfuryl mercaptan dissolved in 250 cc. of ether. A vigorous reaction ensued, and because of the separation of the white heavy intermediate (see Reaction 111), 100 cc. of ether was added. After allowing the mixture to come to room temperature, it was refluxed for three hours on a water-bath.

To the mixture, which was then permitted to come to room temperature, was added dropwise and with vigorous stirring, a solution of 93.8 g. (0.4 mole) of β-chloro-ethyl *p*-toluenesulfonate in 150 cc. of ether. The resulting mixture, subsequent to a two-hour period of reflusing on a water-bath, was cooled and then hydrolyzed by 250 cc. of water containing 30 cc. of sulfuric acid. The hydrolysate was transferred to a separatory funnel and 500 cc. of water was added to dissolve the magnesium *p*-toluenesulfonate. The ether layer (after washing with water and drying with sodium sulfate) was distilled at atmospheric pressure to remove the ether and most of the ethylene chlorobromide. The β-chloro-ethyl furfuryl sulfide was obtained by vacuum distillation as a colorless liquid boiling at 128° (5 mm.). The yield was 32 g. or 90%. It distils at 5 mm. without decomposition, but begins to darken after standing for a few days and decomposes on long standing The chlorosulfidehas a pronounced odor which is very disagreeable at high concentration, but in dilute form it is pleasant and resembles somewhat a mustard odor. A saturated solution in water at 30° contains 0.123% of the sulfide; d_{30}^{30} 1.1914; n_{D}^{30} 1.5200.

Anal. Calcd. for C_7H_9OClS: S, 18.13; Cl, 20.11. Found: S, 17.41, 17.49; Cl, 20.26, 20.09.

γ-Chloropropyl Furfuryl Sulfide, $C_4H_3OCH_2S(CH_2)_3Cl$.—This chlorosulfide was prepared after the method just described for the synthesis of the p-chloro-ethyl homolog. From a 0.1-mole run using 3 g. of magnesium, 11 g. of ethyl bromide, 11.4 g. of furfuryl mercaptan and 49.6 g. of y-chloropropyl p-toluenesulfonate, the yield of γ-chloropropyl furfuryl sulfide distilling at 135° *(5 mm.)* was 15 g. or 79%. It is a colorless liqyid with an odor similar to that of p-chloro-ethyl sulfide, and although it darkens on standing it is more stable than the p-chloro-ethylsulfide; d_{30}^{30} 1.1687; n_{D}^{25} 1.4740.

Anal. Calcd. for $C_8H_{11}OClS$: S, 16.80; Cl, 18.63. Found: S, 16.38, 16.26; Cl, 18.59, 18.59.

Physiological **Tests**

The γ-chloropropyl furfuryl sulfide when applied to the skin in undiluted form produces no skin irritation.

Several preliminary qualitative tests were carried out with the β-chloro-ethyl furfuryl sulfide. When applied to the skin in undiluted form a red spot appeared in two to three hours, and with some men, large deep blisters developed in five to eight hours. Of the five who were tested in this Laboratory, three developed burns very like those of mustard gas, whereas

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[5] The most recent reference is that of Gilman and Heck, ***Ber.,*** 62, 1379 (1929). From this all previous references may be traced.

the other two had deep red blotches which persisted for several months.[6]

In a more exact study, six men were selected for the test which was run with a 0.5% mustard gas control. The mustard gas caused a blister on all subjects, while our chlorosulfide was negative up to 2%. A 3% solution caused redness and slight itching. A 5% solution caused a blister which was equal in nearly every case to the blister caused by a 0.5% solution of mustard gas. It also caused itching comparable to mustard gas. Carbon tetrachloride was used as a solvent for both compounds. It is quite probable that the furfuryl sulfide is more effective than these results indicate, because the tests were carried out with a sample that had undergone partial decomposition. Because of this decomposition no toxicity tests were made.

The authors wish to thank the Miner Laboratories of Chicago for liberal supplies of furfural, and those who helped carry out the several tests.

Summary

Directions are given for the preparation of β-chloro-ethyl furfuryl sulfide and γ-chloropropyl furfuryl sulfide in good yields. The β-compound in agreement with other results has a pronounced vesicant action, whereas the γ-chlorosulfide is without vesicant action.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

ALPHA-METHYL-GAMMA-TETRAHYDRO-2-FURYLPROPYLMAGNESIUM BROMIDE

BY HENRY GILMAN AND JOSEPH B. DICKEY

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Introduction

In extension of studies concerned with furan compounds, it was quite natural for us to turn to the preparation of organomagnesium halides synthesized from furan types, primarily with a view to an interpretation of other furan reactions. An astonishingly small number of such investigations has been made, undoubtedly because of the inaccessibility of halogen furan compounds and the relative inertness of the halogen in many of these compounds. Moureu, Dufraisse and Johnson[1] prepared furylacetenylmagnesium bromide $C_4H_3OC{\equiv}CMgBr$, by an indirect method in-

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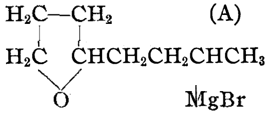
[6] Some tests were carried out with the assistance of Professor M. D. Helser (to whom grateful acknowledgments are made) on hogs, in connection with the possible utility of these and other compounds for the marking of hogs. When applied in undiluted form to the skin of hogs twelve hours before killing, intense red spots remained on the skin of the animals after removal from the depilatory bath. However, no blisters developed.

[1] Moureu, Dufraisse and Johnson, Ann. *chim.*, 7, **1 (1927).**

volving the reaction between ethylmagnesium bromide and furylacetylene, which is prepared with unusual difficulty and in depressingly low yields after a series of transformations. Allen and Rosener[2] were unsuccessful in their attempts to prepare a Grignard reagent from 2,3,5-triphenyl-4-bromofuran. This is understandable in view of the extreme inertness of the bromine even toward hot alcoholic potash. Fenton and Gostling[3] reported no appreciable reaction between 5-bromomethylfurfural and magnesium in benzene.

The organomagnesium halide which we have prepared is readily obtainable by standard reactions which start with furfural. This aldehyde is condensed to furfuralacetone,[4] which is then catalytically reduced by the method of Kaufmann and Adams[5] to a-methyl-y-tetrahydro-2-furylpropanol. There was no difficulty in converting this carbinol to the corresponding bromide, and the Grignard reagent is prepared from the bromide with great ease and in excellent yields (94%). The organomagnesium halide so prepared, a-methyl-y-tetrahydro-2-furylpropylmagnesium bromide (A) has been characterized by appropriate derivatives.


(A)

Experimental Part

The furfuralacetone, prepared after the directions of Leuck and Cejka,[4] was obtained in the yields described by them. However, we could not equal the yields described for the preparation of α-methyl-γ-tetrahydro-2-furylpropanol. Our yields varied from 15 to 25% when 55.0 g. (0.404 mole) of furfuralacetone in 150 cc. of 95% ethyl alcohol was catalytically reduced with 1.0 g. of the platinum catalyst. Several runs were made with varying small quantities of ferrous chloride as a promoter, but there was no essential alteration in yield. The promoter was tried in the hope that the catalytic reduction, which proceeds with ease, might be restricted, because it is possible to have a miscellany of reduction products with a compound like furfuralacetone. Possibly a part of our difficulty lies in incomplete fractionation. Whatever the cause, it is very gratifying to report that unpublished results on the catalytic reduction of furylacrolein by the method of Adams and Bray[6] have consistently given yields which are several per cent. in excess of those reported by them. In this latter reduction, absolute ethyl alcohol was used as the medium, and there is a possibility that such alcohol might improve the yield of α-methyl-γ-tetrahydro-2-furylpropanol. The ready accessibility of α-tetrahydro-2-furylpropanol, the high yields of chloride from this, and the high yields of Grignard reagent from the chloride make this a better organomagnesium halide for synthetic purposes.

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[2] Allen and Rosener, THIS JOURNAL, 49, 2110 (1927).

[3] Fenton and Gostling, J. Chem. *Soc.*, 79, 807 (1900).

[4] Leuck and Cejka, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1927, Vol. VII, p. 42.

[5] Kaufmann and Adams, THIS JOURNAL, 45, 3029 (1923).

[6] Adams and Bray, *ibid.*, 49, 2101 (1927).

Benzoate of a-Methyl-y-Tetrahydro-2-Furyl-Propanol, $C_4H_7OCH_2CH_2CH(CH_3)OCOC_6H_5$.—The butanol was characterized by the preparation of the benzoate. This ester was obtained in a 72% yield by refluxing the carbinol with benzoyl chloride in benzene. It is a colorless, stable liquid, with a sharp taste and with no appreciable odor. The boiling point is 164–166° (3 mm.).

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.53; H, 8.12. Found: C, 72.20, 72.35; H, 8.05, 8.02,

a-Methyl-y-tetrahydro-2-furylpropyl Bromide, $C_4H_7OCH_2CH_2CH(CH_3)Br$.—This bromide was obtained in a 59.8% yield by saturating a solution of 20.4 g. (0.141 mole) of the carbinol in 20 cc. of anhydrous benzene with hydrogen bromide.[7] The bromide distils at 79.5–80° (4 mm.) as a clear, colorless liquid, of sweet odor and sharp taste. It is insoluble in water, but soluble in the more common organic solvents; d^{20}_{20} 1.2000; n^{20}_{D} 1.4719.

Anal. Calcd. for $C_8H_{15}OBr$: Br, 38.6. Found: Br, 38.03, 38.10.

a-Methyl-y-tetrahydro-2-furylpropylmag Bromide, $C_4H_7OCH_2CH_2CH(CH_3)MgBr$.—Following the directions of Gilman, Zoellner and Dickey,[8] the reaction was started by adding a few drops of the undiluted bromide and a crystal of iodine to 2.39 g. (0.0986 atom) of 30–80 mesh magnesium in 10 cc. of ether. Then the remainder of the bromide, totaling 18.5 g. (0.0896 mole) in 35 cc. of ether was added over a period of one and one-half hours. Subsequent to addition of the halide, the mixture was refluxed for one hour. Titration by the method of Gilman, Wilkinson, Fishel and Meyers[9] showed the yield to be 91.5%. In another experiment of 0.02 mole size, the yield was 94%.

The Grignard solution gave a beautiful blue color when a small aliquot was treated after the color test directions of Gilman, Schulze and Heck[10] for reactive organometallic compounds.

α-Methyl-γ-tetrahydro-2-furyl-butyro-α-Naphthalide, $C_4H_7OCH_2CH_2CH(CH_3)CONHC_{10}H_7$-$\alpha$.[11]—The a-naphthalide was prepared in accordance with the directions of Gilman and Furry[12] from the Grignard reagent and α-naphthylisocyanate. It melts[13] at 109.5–110°.

Anal. Calcd. for $C_{19}H_{23}O_2N$: C, 76.72; H, 7.77. Found: C, 76.06, 76.00; H, 8.29, 8.23.

a-Methyl-y-tetrahydro-2-furylbutyric Acid, $C_4H_7OCH_2CH_2CH(CH_3)CO_2H$.—The acid was prepared by the carbonation of the organomagnesium bromide, in accordance with the directions of Gilman and Parker.[14] The yield of pure acid, distilling at 104–106° (0.2–0.3 mm.), was 59% (calculated on the RMgBr compound). It is a water-

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[7] No study was made of optimal conditions for the preparation of the bromide. Because our chief interest was to procure the bromide free of carbinol, this saturation was extended over several days. Unquestionably the time can be drastically reduced because the first saturation, in a cooling mixture, was accompanied by a somewhat vigorous reaction.

[8] Gilman, Zoellner and Dickey, THIS JOURNAL, 51, 1576 (1929).

[9] Gilman, Wilkinson, Fishel and Meyers, *ibid.*, 45, 150 (1923).

[10] Gilman and Schulze, *ibid.*, 47, 2002 (1925); Bull. *soc. chim.*, 41, 1479 (1927). Gilman and Heck, *Rec. trav. chim.*, *48,* 193 (1929); *Ber.*, 62, 1379 (1929).

[11] The authors are indebted to Nina B. St. John for the preparation of this compound.

[12] Gilman and Furry, THIS JOURNAL, 50, 1214 (1928).

[13] The temperatures recorded in this paper are uncorrected.

[14] Gilman and Parker, THIS JOURNAL, 46, 2816 (1924).

white, stable liquid of a sharp taste and disagreeable odor, and is slightly soluble in water; d_{20}^{20} 1.0401; n_{D}^{20} 1.4528.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.74; H, 9.37. Found: C, 62.50, 62.35; H, 9.50, 9.46.

Summary

α-Methyl-γ-tetrahydro-2-furylpropylmagnesium bromide is obtainable in excellent yields from the corresponding bromide which is accessible, in turn, from furfural. This organomagnesium halide is one of the unusually small number of the furan type so far reported, and probably the first to be obtained by a direct reaction. It has been characterized by appropriate derivatives.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY, AT WASHINGTON SQUARE COLLEGE]

CRYSTALLINE MONOMETHYLDIETHYLMERCAPTOGLUCOSE

BY PHILIPPOS E. PAPADAKIS

RECEIVED FEBRUARY 21, 1930 PUBLISHED MAY 8, 1930

The author has had occasion to prepare pentamethyldiethylmercaptoglucose using Fischer's[1] method for the formation of diethylmercaptoglucose and a combination of Haworth[2] and Freudenberg's methods for the methylation process as described by Levene and Meyer.[3]

In some experiments, instead of following Levene and Meyer's procedure, which favors the formation of the polymethylated product, the following method was adopted. The dimethyl sulfate, three times the required amount, was placed in a three-necked flask; the flask was provided with an efficient stirrer, a reflux condenser and a large separatory funnel; the diethylmercaptoglucose was suspended in the sodium hydroxide, which was placed in the separatory funnel, and thence was allowed to flow into the flask gradually. The temperature was kept at 67°.

The methylated product was extracted by ether. After the ether was evaporated the remaining brown sirup which was supposed to contain the polymethylated product was very little in quantity. From the brown sirup, however, a crystalline substance was obtained which was recrystallized from absolute alcohol and gave a melting point of 156°. These crystals were kept for future reference.

Besides these crystals it was observed that during the ether extraction *a* solid substance was going into suspension in the ether layer. From this solid substance some unmethylated mercaptoglucose was extracted by boiling ether. The residue had a melting point between 155 and 160°.

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[1] E. Fischer, Ber., 27, 673 (1894).

[2] W. N. Haworth, J. Chem. *Soc.*, 107, 11 (1915).

[3] Levene and Meyer, J. Biol. Chem., 67, 176 (1926).

It had an appearance similar to the unmethylated product, but a different melting point. At this point it was decided to subject this substance to further methylation.

These crystals as well as more diethylmercaptoglucose were further subjected to methylation. This time the procedure described by Levene and Meyer was followed. The results with respect to the polymethylated diethylmercaptoglucose were more satisfactory, but the yield was smaller than that of Levene and Meyer. On account of this, the water layer after the ether extraction of the polymethylated product was placed aside for later investigation. After some days it was observed that a precipitate was formed which was not soluble in water. This substance was dissolved in chloroform and alcohol and left to stand overnight. In the alcohol layer were formed thin silky fibrous crystals which were recrystallized three times from absolute alcohol and gave a melting point of 156–157'. The results of micro analysis of this substance are given later.

The ether extract which contained the polymethylated diethylmercaptoglucose had dissolved some of the above substance. On evaporation of the ether and distillation of the polymethylated mercaptoglucose under reduced pressure, a substance remained in the distilling flask which always charred at higher temperature. This residue before charring was dissolved in chloroform and from the dark oily liquid after long standing crystals were obtained which were recrystallized from hot alcohol and gave a melting point of 152"; on further recrystallization they gave a melting point of 156–157'.

The analyses for carbon, hydrogen, sulfur, ethyl and methyl radicals were made according to F. Pregl's micro analytical methods at the Rockefeller Institute for Medical Research by Mr. D. Rigakos. The results are indicated in the following Table.

TABLE I

ANALYTICAL DATA FOR MONOMETHYLDIETHYLMERCAPTOGLUCOSE

Sample. mg.	Weighed, mg		Calculated for	%	Found. %
3.630	AgI	8.440	1 Me, 2 Et	24.35	24.13
3.350	$BaSO_4$	5.195	S	21.28	21.30
4.450	H_2O	3.30	H	8.05	8.28
	CO_2	7.185	C	43.97	44.03
4.930	H_2O	3.615	H	8.05	8.20
	CO_2	7.920	C	43.97	43.81

These results indicate that the partially methylated diethylmercaptoglucose is the monomethyl derivative.

The author wishes to express his thanks to Professor W. C. MacTavish of New York University at Washington Square College and to Professor John M. Nelson of Columbia University for their constant interest in his research. The author is indebted to Mr. Rigakos for the analytical part of this work.

Summary

Monomethyldiethylmercaptoglucose has been isolated as a by-product from the preparation of pentamethyldiethylglucose.

NEW YORK CITY

NOTE

The Use of Aryl Esters for the Preparation of **Amides** and Derivatives of Urea. - During my investigations with Professor W. A. Noyes concerning optically active diazo compounds, the preparation of N-substituted acid amides was frequently necessary in order to separate certain stereoisomeric amines. They were also required as intermediate products in obtaining the diazo compounds. These preparations have been accomplished, usually, by condensation of the ethyl esters of the organic acids concerned with the amine by means of refluxing for several hours. In this condensation it has been observed that in general the esters of phenol or substituted phenols react more rapidly and at lower temperatures than the corresponding ethyl esters. Occasionally a considerable development of heat was noticed. Isolated examples of this behavior may be found in the literature. Diphenyl carbonate hss been recommended as especially adapted for the preparation of urea, since it reacts very readily with ammonia even at water-bath temperature.[1] The corresponding ethyl ester reacts only by heating at 180° for a long time in a sealed tube.[2]

It has been recorded in the literature that guaiacol carbonate behaves with ammonia and amines in the same manner as diphenyl carbonate, forming urea or its N-substituted derivatives, instantly.[3] Dr. Noller, in this Laboratory, has recently prepared diphenylcarbazide $(C_6H_5NH\text{-}NH)_2$-CO, from phenylhydrazine and guaiacol carbonate.[4]

It has now been found that diphenyl carbonate reacts as readily with aniline, bornylamine and other amines as it does with ammonia. A mixture of bornylamine and diphenyl carbonate melts with an evolution of heat. By warming on the water-bath the reaction will be finished after five to ten minutes, with solidification. In the use of diethyl carbonate no action could be obtained even by heating to 180° in a sealed tube for four hours.

It has also been found that diphenyl oxalate shows a behavior very similar to the diphenyl and guaiacol carbonates, being much more reactive than the diethyl ester. Bornylamine and diphenyl oxalate react at 80° within a few minutes, forming dibornyloxamide, while the reaction with diethyloxalate requires refluxing for three to four hours. Also, the formation of

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[1] Hentschel, *Ber.*, 17, 1286 (1884).

[2] Natanson, *Ann.*, 98, 289 (1856).

[3] Cazeneuve, Bull. *soc. chim.*, [3] 15, 714 (1896).

[4] Private communication.

oxanilide and other derivatives proceeds more rapidly when using the phenyl ester.

By the use of the aryl esters a method of obtaining N-substituted amides is available which is much more suitable than the one employing ethyl esters, ordinarily used. The phenol formed by the reaction can be removed easily by the addition of aqueous sodium hydroxide and filtering off the amide from the soluble phenolate. In some cases steam distillation of the phenol is possible. Aryl esters are easily obtained by treating a mixture of the phenolic compound and the free acid with phosphorus oxychloride. Of course, for preparation of the carbonate, phosgene is used.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
ULRICH HEUBAUM

RECEIVED DECEMBER 10, 1929
PUBLISHED MAY 8, 1930

COMMUNICATIONS TO THE EDITOR

PHOTOSENSITIZATION BY AMMONIA

Sir:

A research by Parkas, Haber and Harteck[1] on the photosensitization of the oxidation of hydrogen and carbon monoxide by means of ammonia is so similar in concept to work at present in progress in this Laboratory that it seems desirable to record immediately our data already obtained.

The illumination of mixtures of ammonia and ethylene at room temperatures and 100° by a mercury arc produces a rapid reduction in pressure which does not obtain with ethylene alone or with ethylene–hydrogen mixtures. It is not, therefore, a mercury resonance-radiation effect but is determined by the ammonia. During the reaction an oil separates which, as it accumulates, slows down the reaction rate.

By analogy with our earlier work[2] with excited mercury one might attribute the pressure change to a polymerization of ethylene under the influence of atomic hydrogen liberated in the photodecomposition of ammonia. We have shown, however, that in the presence of ethylene the normal decomposition of ammonia is much retarded. In the presence of 15 cm. of ethylene the photodecomposition of 5 cm. of ammonia is reduced to 5% of the normal rate. A further distinction from the work with excited mercury is found when hydrogen is present in the reaction system. With hydrogen, ethylene and ammonia an equally rapid pressure decrease occurs on illumination but no hydrogen disappears. Hence, even in presence of hydrogen, the reaction is one of polymerization.

[1] Parkas, Haber and Hartcck, *Naturwissenschaften*, **18**, 266 (1930).

[2] Taylor and Hill, THIS JOURNAL, 51, 2922 (1929).

Over a wide concentration range the rate of reaction is independent of the ethylene concentration and increases with increasing ammonia concentration. The temperature coefficient is low and of the order of 1.03 per 10°. The quantum yield is of the order of unity if that for ammonia is taken as 0.2.

We are dealing, therefore, with a polymerization of ethylene photosensitized by ammonia. The retarded decomposition of the ammonia is of very great importance since it has been assumed of molecules showing predissociation spectra that absorption leads to decomposition without collision within $\sim 10^{-12}$ sec. In our pressure range (5–15 cm.) the collisions occur only after $\sim 10^{-9}$ sec. It is, therefore, difficult to account for the retarded ammonia decomposition on the present accepted ideas concerning predissociation. We are pursuing this work.

Frick Chemical Laboratory
Princeton University
Princeton, New Jersey

Hugh S. Taylor
H. J. Emeléus[3]

Received April 17, 1930
Published May 8, 1930

A CAPILLARY MERCURY-VAPOR LAMP

Sir:

A simple mercury-vapor lamp of high intensity has been developed in this Laboratory. It is cheap and easily constructed so that one can afford to operate it at a considerable overload for photochemical investigations. These lamps have been used in several different researches and they have been tested by friends in other laboratories.

The lamp is made from clear fused quartz tubing, 10 cm. long with an inside diameter of 1.5 mm. and an outside diameter of 4 mm. Three bulbs are blown, the first 15 mm. from the top, the second 20 mm. and the third 40 mm. from the top. The ends are constricted to enclose the tungsten electrodes, 0.75 mm. in diameter. The upper electrode is sealed in with fused silver chloride, the proper amount of pure mercury is introduced and the second electrode is sealed in with silver chloride. The electrodes are connected to copper wires and covered with de Khotinsky cement, which insulates the wires and makes the seals gas tight. The upper electrode is long enough to reach through the uppermost bulb and nearly to the second bulb. The mercury reaches to the bottom of the uppermost bulb and the remaining air space serves as an expansion chamber.

The lamp is held in a vertical position over a funnel and a water jet is mounted just above it. It is started by adjusting the resistance in series with the lamp, closing the circuit (500 or 110 volts d. c.), and separating the mercury thread between the second and third bulbs (20 mm. apart)

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[3] Commonwealth Fund Fellow.

with a small Bunsen flame or an electric heating coil. As soon as the arc strikes, a stream of water is immediately run over the lamp. Soft water or distilled water should be used. The lamps operate satisfactorily on 3 to 5 amperes with a potential drop of 60 to 300 volts. The upper electrode is positive.

The intensity varies with the individual lamps but the intensities on the different lines have been found to be approximately ten times or more as great as those obtained with commercial lamps operating under normal conditions. Uranyl oxalate has been decomposed at the rate of 0.5 g. of oxalic acid per minute using a cylindrical cell around the lamp. Raman effects have been observed with shorter exposures than are required with other lamps.

Some lamps have given fifty hours of service but when operated at very high intensity they usually fail after ten hours. Many lamps have shown but little decrease in intensity over the first few hours.

The lamp described here is particularly useful for illuminating spectrometer slits or for irradiating small volumes of material. Experiments are being continued also with metals other than mercury.

LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON WISCONSIN
LAWRENCE J. HEIDT
FARRINGTON DANIELS

RECEIVED APRIL 29, 1930
PUBLISHED MAY 8, 1930

NEW BOOKS

Einführung in die theoretische Wutschaftschemie. (Introduction to the Principles of Economic Chemistry.) By Dr. Phii. RUDOLF KOETSCHAU. Theodor Steinkopff, Residenzstrasse **32,** Dresden-Blasewitz, Germany, 1929. xii + **155** pp. 13 figs. 15.5 × 23.5 cm. Price, unbound, RM. 12; bound, RM. 13.50.

Scientists in the past, starting from the known or central truth of phenomena, have tended to explore outward almost exclusively along the straight line of their own discipline. Chemists stuck to chemistry, and biologists to biology.

In the last few decades, however, there has been a steady obliteration of boundary lines, and a continually increasing cooperation among specialists. Research in the no man's land between the natural sciences is bringing astounding results, now partly embodied in texts on physical chemistry, biochemistry, astrophysics and the like. The social scientists have likewise exchanged results among themselves. But the natural sciences and the social sciences have generally been thought in the main to lie in different strata.

Dr. Koetschau does not think so. In fact, he believes that a new science ought to be recognized: economic chemistry or chemical economics. It conceivably might be the forerunner of a host of hybrid sciences—economic botany, economic geology, etc. All such new sciences need analytical working tools, concepts unequivocally defined. Such Dr. Koetschau's book purports to give for economic chemistry.

It quite naturally divides itself into three main parts: an introductory essay on epistemology, a description of certain alleged economico-chemical concepts for which sundry symbols are coined, and a manifesto consisting of twenty theses or tentative generalizations, presented in the approved medieval manner for verification, modification or nullification.

The first part (pp. 1–29, 55–65) endeavors to prove that economics and chemistry as sciences lie on the same plane, that their concepts are germane, and that, therefore, cross-fertilization is possible. The familiar contentions of the Neo-Kantians, especially Windelband, Rickert, and Cassirer, are adduced. The natural sciences and the social sciences both use the quantitative-mathematical method of fixing the orbit of their concepts, and in so far as that is true, their concepts are not contradictory, but correlative. The arguments of Oppenheim in his "Natural Classification of Sciences" are also used. In short, no gulf exists between the natural and the social sciences. Their laws differ in degree, not in kind. In other words, it is possible for a science of theoretical economic chemistry to exist.

The second part (pp. 29–55, 65–86) describes four sets of concepts, supposedly coordinate, which lie in the domain of economic chemistry. The first consists of the totality of chemical and physico-chemical processes in so far as they have or can have economic significance. The symbol "ch" is used to designate all the laws of homogeneous and heterogeneous chemical equilibria for all states of aggregation—the law of mass action, the Le Chatelier principle, the phase rule, etc. The second set of concepts comprises (p. 45) the totality of changes of matter which are purposively manipulated to take place in definite amounts during a set period of time. Chemical processes can now be represented by vectors, which, when combined, show a definite quantum of salable product. All the principles which guide the chemical technologist, such as the tendency to substitute continuous for batch processes, are designated by the Greek letter χ. The third set of concepts, represented by the letter w, comprises the numerous laws (sic! p. 50) which economics has discovered; laws which have reference to demand, supply, value, credit, and so on; laws which, by assuming that business is run to maximize profits, formulate the interaction of the forces at work in a given system of interdependent economic equilibria, and evaluate their benefit or harm to society as a whole. A superficial attempt is made to utilize the results of statisticians and of mathematical economists such as Schumpeter and Pareto. The fourth set of concepts, designated by the Greek letter τ, logically it ought to come third, represents all those principles of procedure, both technological and commercial, which are commonly implied in the phrase, "the present state of the arts." τ stands for all those practices of sound business administration, plant location, process costing, etc., which Mr. Chaplin Tyler has so ably elucidated in his "Chemical Engineering Economics."

Thus the transition is made from pure chemistry via chemical technology and business technique to economics. A science is mapped out which is designed to coordinate the efforts of the chemist seeking the truth for its own sake, the endeavors of the chemical engineer interested primarily in the technological perfection and dovetailing of the productive processes, the energies of the business man worshiping profits, and the theoretical and practical programs of the political economist endeavoring to maximize social income and general prosperity.

The third part of Dr. Koetschau's book consists of twenty theses, which in part recapitulate, and in part trace interrelationships between, the four sets of concepts. The result, as one might expect, is meager. Chemists who go into business must keep in mind that chemical processes must be adjusted so as to earn maximum profits. Such are the platitudes to which the theses can be reduced, so that one has the distinct feeling of being all dressed up in formidable terminological clothes, with no place to go.

Finally, attention must be called to the extraordinary amount of reading which has been epitomized in the book. Over 210 authors are cited, twenty of them more than five times, in about 130 pages of text. The volume shows not only ingenuity in the coining and defining of terms, but also an heroic, even if to the skeptical reader an unsuccessful, attempt to found a new science.

THEODORE J. KREPS

The American Illustrated Medical Dictionary. A Complete Dictionary of the Terms used in Medicine, Surgery, Dentistry, Pharmacy, Chemistry, Nursing, Veterinary Science, Biology, Medical Biography, etc., with the Pronunciation, Derivation, and Definition. By W. A. NEWMAN DORLAND, A.M., M.D., F.A.C.S., Lieut. Colonel, M.R.C. U. S. Army, Member of the Committee on Nomenclature and Classification of Diseases of the American Medical Association; Editor of American Pocket Medical Dictionary. Fifteenth edition, revised and enlarged with the collaboration of E. C. L. MILLER, M.D., Professor of Bacteriology and Biochemistry, Medical College of Alabama. W. B. Saunders Company, Philadelphia, 1929. 1427 pp. 16 × **23** cm.

This fifteenth edition of a volume first issudd in 1900 has been amplified and brought up to date by the inclusion of many new terms, and is reset from new type. The reasons for its popularity may easily be understood. The typography and the arrangement of material are excellently chosen. making it convenient to consult and read. Some 70,000 of the terms of medicine and related arts and sciences are contained in it. The definitions are brief, encyclopedic discussions being happily absent. The many illustrations are for use rather than ornament; and the hundred or so tables are admirably selected, sufficiently complete and carefully arranged, whereby the user's time and effort are economized.

Many terms in the borderland subjects of medicine have been included, and here lies its value to chemists, for not only may the common terms of chemistry be found but also the words and phrases of modern biological science with which the chemist of today is increasingly concerned.

Although in the introduction it is stated that the nomenclature adopted by the American Chemical Society (among others) has been followed, this is not always true, nor is the chemistry invariably as modern as would appear desirable. Soda, for example, is defined as "a loose term which generally refers to sodium hydrate, (NaOH)"; and the spelling hydrochinone is preferred to the commonly accepted form hydroquinone. Nevertheless, for its borderline terms alone it is valuable and should be available to every student and worker in the biological sciences.

WILLIS A. BOUGHTON

Handbook of Chemical Microscopy. Vol. I. By ÉMILE MONNIN CHAMOT, B.S., Ph.D., Professor of Chemical Microscopy and Sanitary Chemistry, Cornell University, and CLYDE WALTER MASON, Assistant Professor of Chemical Microscopy, Cornell University. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1930. xiii + 474 pp. 162 figs. 15.5 × 23.5 cm. Price, $4.50.

"The present Handbook of Chemical Microscopy is an attempt to present in logical and concise form the principles and methods involved in practical microscopy. * * * Altho based on 'Elementary Chemical Microscopy,' the present book has been entirely rewritten, and expanded in all sections. * * * Much of the material here compiled and discussed for the first time in book form is of paramount importance to all microscopists * * *. Volume I has been confined to a discussion of optical principles of instruments, manipulative methods of general application and the observation of physical and physico-chemical phenomena." The purposes indicated in the preceding extracts from the preface have been well carried out. The first chapters discuss the microscope in general, and the microscope for chemical use in particular. More attention might well have been given to the petrographic microscope, since the more accurate measurement of properties, as opposed to merely qualitative observation, is becoming of increasing importance in general work. Subsequent chapters give adequate discussions of illumination methods, ultramicroscopy and photomicrography and much detailed information is given of special manipulative procedures. The determination of melting points with the aid of a hot stage surely is not inherently so inaccurate a procedure as is implied in the footnote to the table on page 211: "Melting points as observed under the microscope are apt to be several degrees lower than those recorded above." A great deal of attention is given to petrographic methods, including the study of crystals in both polarized and non-polarized light, and, on the whole, the discussion is unusually clear. The difficult subject of interference figures and their interpretation is well treated. The difference between the "Becke line" and the bright line obtained with axial illumination is not clearly brought out, and in subsequent discussion leads to some confusion. In practice the Becke test is used far less than the axial illumination method, and the remarks on page 374 concerning their relative accuracy apply equally well to anisotropic substances. In the footnote on page 376 mention should also be made of the publications of Winchell, "The Optic and Microscopic Characters of Artificial Minerals," University of Wisconsin Studies in Science No. 4, and Fry, "Tables for the Microscopic Identification of Inorganic Salts," Bull. No. 1108, U. S. Dept. of Agriculture. The sentence, middle of page 377, beginning, "If the material is uniaxial * *," is misleading; the index for the ordinary ray, ω, is determinable on every grain, but only when it is oriented properly with respect to the polarizer. A grain cannot lie in such a manner as to show β, and appear isotropic, as implied near the top of page 378. It does not necessarily follow from $(\gamma - \beta) > (\beta - \alpha)$ that the grain is positive, as stated on page 378; this is a first approximation that does not hold when the birefringence is large.

The increased scope of this book as compared with "Elementary Chemical Microscopy" will greatly add to its value both as a textbook and for general reference, and it is encouraging to think of a generation of chemists equipped to make use of the powerful aid of the microscope both to supplement and to replace chemical analysis. The illustrations are well done. The reviewer will look forward with great interest to the appearance of Vol. II.

GEORGE W. MOREY

Colloid Symposium Monograph. Vol. VI. Papers presented at the Sixth Symposium on Colloid Chemistry, University of Toronto, June, 1928. Edited by HARRY BOYBR WEISER, Professor of Chemistry, The Rice Institute. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1928. 346 pp. Illustrated. 16 X 23.5 cm. Price, $6.50.

Colloid Symposium Annual. Vol. VII. Papers presented at the Seventh Symposium on Colloid Chemistry, Johns Hopkins University, June, 1929. Edited by HARRY BOYER WEISER, Professor of Chemistry, The Rice Institute. John Wiley and Sons, Inc., New York, 1930. viii + 300 pp. Illustrated. 15.5 × 23.5 cm. Price, $4.50.

The annual Colloid Symposia have been foci of research enthusiasm and the annual volumes containing the papers delivered at these Symposia have been and are important factors in the publication of American chemical research. The articles thus published are not only useful, but in marked contrast with much of our periodical literature in chemistry they are interesting. This is due in part to the great variety of subjects covered under the caption of Colloid Chemistry, but chiefly to the fact that these articles are often not merely the report of a single detached investigation but are a readable summary of all of the author's researches and those of others in the field.

The two most recent volumes (VI and VII), containing the papers presented at the annual Symposia on Colloid Chemistry in 1928 and 1929, are particularly varied and interesting in their contents. It is perhaps invidious to select particular articles for special mention, for such a selection is at once highly subjective and arbitrary. The reviewer cannot, however, refrain from calling attention to the brilliant, trenchant and interesting introductory address in the 1928 volume, entitled "Living Matter," by Sir William B. Hardy, and to the very instructive articles in the same volume, by Alfred J. Stamm on "The Structure of Softwoods" and by A. Baird Hastings on "The Rôle of Hemoglobin in the Blood."

Again in the 1929 volume, the paper by A. Frumkin, entitled "Significance of the Electrocapillary Curve," is an unusually careful and exhaustive study of this difficult subject. The article by Donald H. Andrews, entitled "Some Evidence on the Nature of Extra-Molecular Forces," appears to offer a promising and novel avenue of attack to this fundamental problem.

Attention should be called to the fact that the name of the publication has been changed in the 1929 volume from Colloid Symposium Monograph to Colloid Symposium Annual, and that the publishing firm has also been changed. The editor and publisher are to be congratulated on their success in reducing the price from $6.50 to $4.50 for practically the same sized volume without any sacrifice of appearance or quality.

ARTHUR B. LAMB

Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Vol. X. Edited by HANS T. CLARKE, with ROGER ADAMS, JAMES B. CONANT, HENRY GILMAN, C. S. MARVEL, C. R. NOLLER and FRANK C. WHITMORE. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1930. vii + 119 pp. 15.5 X 23.5 cm. Price, $1.75.

Inasmuch as the Editorial Board of Organic Syntheses is preparing a revised collection of the material presented in the first nine volumes, volume ten is treated as the first number in the second decade of the series and contains no index to preceding volumes. "Otherwise no departure has been made from the general plan adopted in recent numbers, beyond the inclusion of a rather greater proportion of organic preparations of a biochemical rather than a strictly synthetic character."

The list of preparations is as follows: acetol, n-amyl benzene, benzenesulfochloride, benzophenoneoxime, bromoacetone, a-bromonaphthalene, casein, *o*-chlorobenzoic acid, dimethylglyoxime, diphenylmethane imine hydrochloride, durene, duroquinone, erucic acid, ethyl fumarate, ethyl oxomalonate, glutaric acid, heptanol-2, lauryl alcohol, malononitrile, methyl oxalate, m-nitroacetophenone, oxalic acid (anhydrous), α-phenyl-β-benzoylpropionitrile, piperonylic acid, 1-propylene glycol, isopropyl lactate, pyromellitic acid, β-resorcylic acid, sodium 2-bromoethanesulfonate, taurine, *l*-tryptophane.

E. P. KOHLER

Der adsorbierende Bodenkomplex und die adsorbierten Bodenkationen als Grundlage der genetischen Bodenklassifikation. (The Adsorbing Soil Complex and the Adsorbed Cations of the Soil as a Basis for the Genetic Classification of Soils.) BY Professor K. K. GEDROIZ, Leningrad. Translated from the second edition of the original Russian by Dipl.-Ing. H. KURON, Assistant in the Agricultural Chemistry Institute of the University of Breslau. Foreword by Professor Dr. Paul Ehrenberg. Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1929. viii + 112 pp. 15.5 × 23.5 cm. Price, unbound, RM. 5.

The author discusses the problem of soil classification and genesis on the basis of the chemical and physical characteristics of the soil colloid. His general conclusion is that such knowledge of soil colloids as we now possess is adequate for a separation of the soils into broad fundamental groups but it is not adequate for a more detailed classification. The great soil groups which he discusses are the chernozem, the solonetz, the podsol and the laterite. If this conclusion were the net result of his discussion the book was perhaps not worth review, but such is not the case. He not only discusses the present state of our knowledge of the genesis of the soils and the composition of the colloids derived from widely varying kinds of soil but he presents a tactful and critical review of the recent literature on the subject, especially that from American and Russian sources.

He presents a coherent theory of the nature of the soil colloid and supports it with cogent theoretical and experimental evidence. His ideas are cautiously expressed and interspersed with regrets because of the frequent lacunae in our information and the paucity of experimental evidence, especially of the relationship of the bases in the soil colloid.

Because of his high position as a soil scientist his ideas are worthy of careful consideration and will be found stimulating even though, as he says himself, many of them are purely speculative and may not receive general acceptance. His consideration of alkali soils is especially important because he, if any one, is in a position to speak with a certain authority in that field.

The book is certainly to be commended to the attention of any one interested in soil research.

HORACE G. BYERS

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[Contribution from the Pacific Experiment Station, Bureau of Mines, United States Department of Commerce]

THE HEAT OF FORMATION OF ZINC OXIDE[1]

By Charles G. Maier[2]

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In spite of the recent careful work of Parks, Hablutzel and Webster[3] on the heat of solution of zinc oxide in hydrochloric acid, the heat of formation of the oxide derivable therefrom by combination with the heat of solution of zinc and the heat of formation of water still remained uncertain by several hundred calories. Parks and co-workers used the results of Richards and Burgess[4] for the solution of zinc, but Richards and Thorvaldson[5] made later determinations in solutions of higher final zinc concentration which differed by 280 calories when brought to comparable conditions of dilution and temperature. This discrepancy is greater than the probable error of available free energy and entropy determinations on zinc oxide.[6,7]

The Pacific Experiment Station of the U. S. Bureau of Mines, in the course of its program of study of the thermodynamic properties of metallurgically important oxides, has carried out redeterminations of the heat of solution of zinc and zinc oxide, in order to arrive at finally acceptable figures. The results, aside from their practical interest with relationship to the metallurgy of zinc, are of some theoretical interest, because they furnish the last link in a comparison of heat of formation, free energy and entropy as derived from widely different experimental methods, and so constitute a direct and many-sided check on the third law of thermodynamics. Although few would now question the utility of this law, it has not as yet attained widespread application to metallurgical processes in this country. The use of the Nernst approximation formula is unsatis-

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[1] Published by the permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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[3] Parks, Hablutzel and Webster, This Journal, 49, 2792 (1927).

[4] Richards and Burgess, *ibid.*, 32, 431 (1910).

[5] Richards and Thorvaldson, *ibid.*, 44, 1051 (1922).

[6] Maier, Parks and Anderson, *ibid.*, 48, 2563 (1926).

Millar, *ibid.*, 50, 2653 (1928).

factory for the prediction of even moderately precise reduction equilibrium, and the precise methods of Lewis and Randall have been unavailable to discussions of oxides, because of dearth of data on these materials.

The experiments here described were performed in a calorimeter with some unusual features. Because of the wide variety of determinations included in the originally projected program, an instrument of considerable flexibility was desired. The apparatus was designed and constructed before the appearance of White's[8] catechistical treatise, and it was first proposed to render the calorimetric process both adiabatic and isothermal. Initial experiments showed, however, that Newton's law of cooling for the completed calorimeter was so accurately obeyed that the maintenance of neither of these conditions was essential for precise work when the duration of the experiments did not exceed a few hours.

The Calorimeter

The unusual features of this calorimeter are the use of a specially constructed and calibrated copper resistance thermometer for measurements of temperature; the equipment of the instrument with a special heating coil of manganin, and an ethyl bromide "boiler" for cooling; and the expedient use of tantalum and bakelite for those portions subject to corrosion. The resistance thermometer is described in detail elsewhere.[9] Details of the other arrangements will be evident from the diagram of Fig. 1.

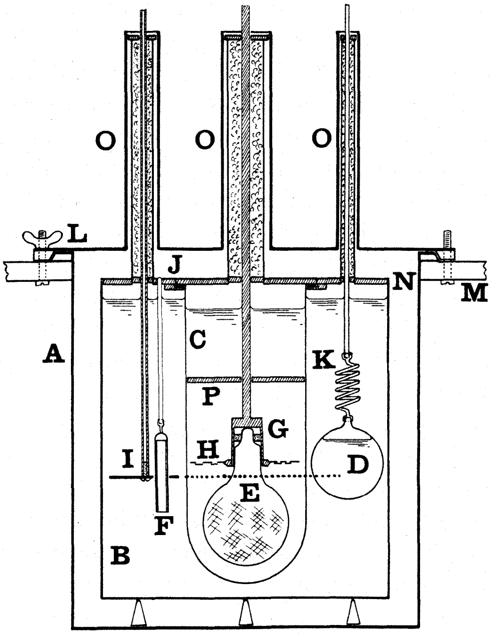

Fig. 1.—The calorimeter.

The outer cylindrical shell A is of heavy sheet copper, heavily gold plated and polished on the inner surface, and is 24 cm. diameter and 26 cm. high. A compression top of similar material has a ground seal at L, and is held in place by twelve screws and wing nuts. From the top extend five copper chimneys O–O–O (three only shown). The calorimeter jar, B, is of 22-gage copper, gold plated and polished externally. It is separated from the shell A by a 2-cm. air space and supported on the bottom by three bakelite cones. A tightly fitting top J is of $^3/_{16}$-inch bakelite, and carries bakelite tubing chimneys, which serve as packing glands. Kapok floss, lightly oiled, serves as a nearly frictionless, yet relatively impervious, packing material.

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[8] W. P. White, Am. Chem. Soc. Monograph 42, Chemical Catalog Co., New York, 1928.

[9] Maier, "Resistance Thermometers for Chemists," submitted to J. *Phys.* Chem., but not yet published.

The mixing chamber, C, is of 10 mil thick tantalum, with roller welded seams, hemispherical bottom and flanged top. It is suspended from the top by a bakelite ring at J.

Reciprocating stirrers I and H are suspended from bakelite tubes or rods. Three such tubes support the copper ring I, which is slit to prevent inductive effects in the thermometer circuits because of its motion in the earth's magnetic field and to render the stirring more effective by lack of symmetry, and which has ports for passing the resistance thermometer F, the "boiler" D, and the manganin heater not shown, but similar in construction to F. The inner stirring head G is of bakelite, and carries the 25-mil. tantalum stirrer H. The three supporting tubes for I, and the single solid rod carrying G are attached to a specially designed "splashless" reciprocator (not shown), carried by *a* cross member of the supporting frame M. The actuating cam motion of the reciprocator is of such a type that the velocity at the top of the stroke is a minimum and a maximum at the bottom. The speed is adjustable to **6**-, **3**- or 2-second cycles, and the stroke is about **5** cm. A bakelite spider P serves as guide for the inner stirrer.

The sample flask E is blown with thin bulb walls, and fixed into the head G with a rubber washer. The attachment of the supporting rod to the reciprocator is a quick release mechanism, enabling the bulb E to be readily smashed against the bottom of the tantalum can while the stirring mechanism is in uninterrupted motion.

The boiler D is of thin-walled pyrex glass, connected by a soldered joint to the helical $^1/_8$-inch copper tube coil K. This coil serves to prevent entrainment of ethyl bromide, and make certain that the vapors issuing from D are at the temperature of the calorimeter. The extension of K through the chimney is of thin glass, with **a** soldered joint.

The frame M, carrying the reciprocator, is suspended above an oil thermostat by a rack and pinion operated through an irreversible worm drive. Under operating conditions the entire shell is submerged approximately to the **O–O–O** level.

The joint L is made oil tight with a thin coating of a heavy paste consisting of zinc oxide and glycerin. The top of the jar is sealed at N by winding several thicknesses of electrician's rubber tape about it with considerable tension. The joint at J is sealed by a coating of heavy stopcock grease.

The tantalum and bakelite construction of this calorimeter has proved highly satisfactory. As compared to a gold or platinum calorimeter, the tantalum shows a decided saving in first cost, and its hardness and toughness render it immune to damage by rough treatment. After breaking numerous flasks upon the bottom, the surface was unmarred, nor has there been the slightest trace of corrosion in 2.7 N hydrochloric acid after a total time of contact extending over several months. The bakelite, too, has proved to be practically unaffected by the solutions used. Because of plastic flow the bakelite top has become slightly concave, but this could have been avoided by better design, or perhaps a ribbed construction. The ease with which fairly good screw threads may be cut in bakelite, combined with its low thermal conductivity and ability to withstand acid corrosion, commends it highly for calorimetric construction where these properties are desired.

Operation of the Calorimeter

The thermostat in which the calorimeter is submerged is at 25 ± 0.005°. The zero of the resistance thermometer temperature scale is 25.006°, and within satisfactory limits of error the resistance thermometer reading gives the thermal head of heat exchange between calorimeter and surroundings. The total heat capacity of the calorimeter with **5** liters of water in the jar, and 0.6 to 0.8 liter of acid in the can, is between 5500 and

6000 calories per degree, and the Newton's law constant is 0.001° per degree per minute. The rate of heat exchange was a linear function of the thermal head to within 0.5%, so that the uncertainty of determination of heat exchange under unit thermal head for an experiment of 100 minutes' duration is about 0.005°, or 2.5 calories.

Because of the exactness with which the heat exchange rate depends upon the thermal head, the ethyl bromide boiler was used only for adjusting the temperature of the calorimeter in these experiments. The operation of the calorimeter, both adiabatically and isothermally, will be described at a later date. The sequence of operations in these experiments was as follows: (1) determination of initial heat capacity, (2) adjustment of temperature by evaporation of ethyl bromide in preparation for the determination of the heat of solution, (3) determination of heat of dissolution, (4) determination of final heat capacity.

The determination of initial and final heat capacities was accomplished electrically. The manganin heater, previously mentioned as similar in construction to the resistance thermometer, had an accurately determined resistance of 100.034 International ohms, as compared with a standard resistance calibrated by the Bureau of Standards. Energy was obtained from thermally insulated polarized alkaline storage batteries, and the current measured every five minutes by observing the drop across a standardized 0.4-ohm manganin resistance (0.399395 International ohms) (kept in the thermostat) with a White double potentiometer. The energy rate was 1 to 1.5 cal. per second. The heating periods of from one to one and a half hours were measured with a stop-watch which had been compared to an astronomically checked chronometer, and during this period the current variation was less than 1%. If I, is the current at any reading time $= I$, $+$ A„ where I_o is a selected approximately mean value, the average square of the current was taken as $I_o^2 + [\Sigma_o^n(2I_o\Delta_n)]/n$ neglecting the Δ_n^2 terms, and the total energy calculated as $I_{av.}^2$ Rt, using 4.184 for the conversion factor from International joules to 15° calories. During the experiments the temperature range was held within approximately one degree from the temperature of the surroundings.

After determination of the initial heat contents, the temperature was brought back to a suitable point in preparation for the dissolution experiment, by applying uniform suction to the outer end of K. With no appreciable difficulty the external pressure in the line to K was maintained constant, resulting in a uniform cooling rate variable from 0 to 1.5 cal. per second.

When the desired temperature (about 24°) had been reached by the contents of the calorimeter, no further evaporation of the bromide was permitted. Thermal equilibrium was attained in four to six minutes. After a preliminary rating period, flask E was smashed at a definite instant and the determination completed in a conventional manner. Points on the temperature curve were plotted on an adequately large scale and the corrected temperature rise was calculated by a graphical Regnault–Pfaundler method. Before the calorimeter was dismantled, the determination of final heat capacity was made. In the calculations correction for the heat content of ethyl bromide evaporated was made at a rate of 0.193, 15° calories per gram, a measured value from experiments to be described elsewhere.

The method of use described above has a number of advantages. Foremost of them is the possibility of direct determination of the temperature coefficient (ΔC_p) of the reaction, a matter of considerable importance in reactions such as the solution of metals or oxides in acid, where the coefficients may be as high as 100 or more calories per degree per formula weight. Moreover, the calibration of the resistance thermometer enters only for the determination of the corrections of heat to a definite temperature; the essential heat determination might be made with a purely arbitrary thermometer scale, that is to say, the direct determination of the electrical energy required to carry the calorimeter and contents through the same temperature rise as that produced by chemical heat. Since random errors in the heat contents determinations are largely magnified in the ΔC_p calculated by difference, the concordance of this quantity per formula weight in a number of duplicate determinations, especially where different quantities of reagents are used, serves as a useful criterion for the authentication of the experimental results. Thus any systematic errors will be ascribable, in a series of determinations showing good concordance in ΔC_p, only to systematic errors in the measurements of electrical energy. In these measurements, repeated checks of the resistances and standard cells used for the electrical measurements showed the uncertainty in energy determinations to be less than one-half per mille.

The Heat of Solution of Zinc Oxide

In the article by Parks and co-workers the statement is made: "Thus the resulting solutions in our experiments had the same concentration of hydrochloric acid and zinc chloride as those obtained by Richards and Burgess." Since water is formed by the action of zinc oxide and acid, but not by metal and acid, it is impossible to have identical initial and final concentrations in the dissolution of oxide and metal, and the authors of the quotation seem to have used identical initial, and not final concentrations. Richards and Burgess dissolved 7.3 g. of zinc in 941.4 g. of hydrochloric acid, $1HCl$ to $20H_2O$, and in these low concentrations the heat of dilution of the solutions, caused by the formation of water, is not great. Because of the large excess of acid used, the heats of dilution of the zinc-containing solutions will not be markedly different from that of pure hydrochloric acid, and may be estimated by the methods of Lewis and Randall[10] to be 27 calories per gram atom of zinc at these concentrations. In the higher concentrations of Richards and Thorvaldson the effect is much larger and cannot be satisfactorily estimated.

In the experiments here described, the "dry process" zinc oxide used had less than 0.05% of impurity, the chief impurity being traces of water-soluble sulfate. The samples were washed, dried and ignited at 600° to decompose traces' of carbonate. A blank heat of wetting determination was made on this material by breaking an evacuated sample bulb containing 41.13 g. of oxide under 850 g. of carbonate-free water in the calorimeter. There resulted a temperature rise of 0.0048°, corresponding to a heat effect of 53 calories per formula weight of ZnO. This heat represents the summation of the heat of wetting of the oxide, the heat to form a saturated solution of oxide in water, and the heat of solution of residual traces of soluble impurities such as sulfate.

No better accuracy than 50 calories per formula weight may, therefore, be claimed for experimental results in which the particle size of zinc oxide is not determined, and since it did not seem practical to separate the various items of heat involved, the following experiments could not be of greater accuracy than this.

TABLE I

SOLUTION OF ZINC OXIDE, RICHARDS AND BURGESS CONCENTRATIONS

	Expt. 1	Expt. 2
Weight of ZnO, g.	8.2396	8.4495
Acid 1HCl:20H_2O, g.	850	850
Heat capacity of calorimeter, cal.	6076.0	5950.4
Uncorrected temperature rise, °C.	0.2473	0.2542
Corrected temperature rise, °C.	0.2462	0.2571
Final temperature, °C.	25.03	25.07
Heat of reaction, cal.	1495.1	1529.8
ΔH at final temperature	−14765	−14781
ΔH_{298}	−14769	−14791

Average ΔH_{298}	−14780
Heat of dilution (calcd.)	27
Corrected heat of solution of ZnO	−14753
R. & B. Heat of solution of zinc (dry gas) at 20°	−30166
Correction to 25°	555
Heat of solution of zinc at 25°	−29611
Heat of formation of liquid H_2O (in soln.) at 25°	−68298
Sum	−97909
Heat of solution of ZnO	−14753
Heat of formation of ZnO at 25"	−83156

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[10] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co, New York, 1923, pp. 92, 96, 477.

In Table I are given the results of two dissolution tests using concentrations similar to those of Richards and Burgess. Through an error, the zinc weighed out in the first experiment was slightly less than should have been used to conform strictly to these concentrations. Because of the relatively low concentration of zinc in the final solution of these first tests, no appreciable error will be introduced because of this. The weights of zinc and acid are reduced to a vacuum basis.

The heat capacities of the calorimeter are 15" calories, and represent the thermal content per degree before the reaction. The heat of reaction calculated, therefore, represents the isothermal heat at the final temperature. Because the dissolution of 8 g. of oxide in 850 g. of acid does not produce a marked total change of heat capacity in this calorimeter, the temperature coefficient of the reaction was calculated rather than determined experimentally as in later experiments. Prom the data of Richards, Mair and Hall[11] the specific heat of the acid used was estimated to be 0.8528 at 25°, and from these data and those of Richards, Rowe and Burgess[12] that of the resulting zinc chloride solution, 0.8618. Then $\Delta C_p = 858.3 \times 0.8618 - (850 \times 0.8528 + 0.1013 \times 9.65) = 13.7$ calories per degree, or 135 calories per formula weight of ZnO. The figure 9.65 for the molal specific heat of zinc oxide is taken from the results of Millar.

In correcting the heat of solution of zinc given by Richards and Burgess as 30,190, 18° calories at 20 to 25°, the difference in heat capacities of final and initial solutions was taken from the work of Richards, Rowe and Burgess (page 1182) as 9 calories for 5 g. of zinc. When this is corrected for the specific heat of the zinc, $\Delta C_p = 8.5$ or 111 calories per formula weight of zinc.

The heat of formation of liquid water was taken as $\Delta H_{298} = -68{,}270$ from Lewis and Randall, with an additional 28 calories as correction for the relative partial molal heat content of the water in the acid solutions used.

The final result of the experiments for the heat formation of oxide, $\Delta H_{298} = -83{,}156$ calories, compared well with the result of Parks and co-workers, $-83{,}244$, although this latter figure would seem to require a correction of 27 calories for the heat of dilution of the solutions creditable to the water formed by the reaction, resulting in $-83{,}271$ calories. The agreement is well within the accuracy of 200 calories estimated by Parks. Because the author's results are somewhat lower than Parks', the discrepancy of 280 calories noted between Richards and Burgess' results, and the presumed more accurate results of Richards and Thorvaldson for zinc metal becomes enhanced in the heat of formation of the oxide, and the desirability of determining the heat of solution of the oxide in more concentrated solutions becomes apparent.

The first experiments at the higher concentrations were failures because

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[11] *Richards, Mair* and Hall, THIS JOURNAL, 51, 725 (1929).

[12] *Richards,* Rowe and *Burgess, ibid.,* **32,** 1176 (1910).

of the formation of insoluble oxychlorides. In one case the oxide was stirred for two days in the acid without complete dissolution, and the final product was a rock-hard cake. Many expedients were tried, but the only one which proved effective was to wet the oxide with water before sealing into the bulb E; when this was done the dissolution could be completed in less than one hour. At these concentrations the thermal effect of water formed by the reaction was not calculable, and subsequent experiments were made with a weighed amount of water added to each sample. Since the heat effect of the reaction is independent of the path, the determination of the heat of dilution of a zinc chloride–hydrochloric acid solution, from the concentration used by Richards and Thorvaldson to the final strength obtained in these experiments, enables the effect not only of the added water, but also of the water formed during the reaction, to be determined.

In order to determine this heat of dilution, 663.59 g. of a solution identical in concentration with Richards and Thorvaldson's final was diluted in the calorimeter with 58.61 g. of water, the stoichiometric equivalent of the concentrations used later for the water added to and formed by the zinc oxide. The uncorrected temperature rise was 0.0355°, the corrected, 0.0337° and the final temperature 24.80°. The initial heat capacity of the calorimeter was 5582.2 calories, the final 5602.5, and ΔC_p per formula weight of zinc in solution 39.6 calories per degree. The heat of dilution is then $\Delta H_{298} = -359$ cal.

In Table II are recorded the results of three successful experiments on the dissolution of zinc oxide at the higher concentrations, the final result of which, $\Delta H_{298} = -17.280$ calories (corrected for dilution), is to be considered in connection with the data of Richards and Thorvaldson, who gave 32,795 calories at 20° for the reaction giving wet gas, or 33,017 for dry gas. Their temperature coefficient was 74 calories per degree for the wet gas reaction, which with appropriate correction becomes 72.6 calories per degree for the dry. Then the heat of dissolution of zinc at 25°, and at these concentrations, is 32,654, which upon conversion to 15° calories is 32,641. By combination with the author's figure at these concentrations corrected for dilution, and using the same heat of formation of liquid water as before, the heat of formation of zinc oxide at 25° from these data appears to be 83,659, as compared to 83,156 from the previous experiments. The discrepancy of 503 calories between the former figure and that calculated from the results of Richards and Burgess is not readily explainable on any basis except that the measurements of Richards and Thorvaldson were not, in fact, more precise than the earlier data, but rather less so. From the free energy determined by cell measurements, and the entropy from low temperature specific heats, Millar calculated by thermodynamic methods $\Delta H_{298} = -83{,}130 \pm 100$, thus confirming the earlier data, rather than the results obtained in concentrations similar to those of Richards and Thorvaldson.

TABLE II

SOLUTION OF ZINC OXIDE, RICHARDS AND THORVALDSON CONCENTRATIONS

	Expt 3	Expt 4	Expt. 5
Weight of ZnO, g.	27 OR74	44 3981	54 0857
Moles of ZnO	0 33289	0 54563	0 66469
Weight of acid, 1HCl:20H_2O, g . .	411 04	673 72	820 73
Weight of water with oxide, g	32 035	52 535	63 930
Initial heat capacity	5370 1	5759 5	5959 8
Final heat capacity .	5608 5	5819 4	0033 3
ΔC_p for the reaction . .	3 8 4	59 9	73 5
ΔC_p per formula weight of ZnO	115	110	112
Uncorrected temperature rise, °C	1 0418	1.5684	1 9087
Corrected temperature rise	1 0530	1 6585	1 9571
Final temperature, °C	25 32	26 03	25 81
Heat of reaction . .	5865 3	9552 1	11663 9
AH at final temperature .	−17619	−17507	−17508
ΔH_{298} (uncorrected for dilution)	−17656	−17623	−17639

Average, −17639 Heat of dilution, −359 Corrected ΔH_{298} −17280.

Heat of Solution of Zinc

Through the courtesy of the New Jersey Zinc Company a sample of "spectroscopically pure" zinc, containing less than 0.001% impurity was obtained, and its heat of solution was measured at the same concentrations used by Richards and Thorvaldson. Because of the extreme purity of the metal, much difficulty was experienced in dissolving it in the calorimeter. Small amounts of platinic chloride added to the hydrochloric acid accelerated the reaction, but did not give acceptable speed. The metal was finally melted in silica, cast into rods, the oxide-containing skin removed on the lathe, and the inner part turned into a thin curl-like ribbon some 0.005″ thick. A sample of the material was weighed, submerged in a nearly neutral 0.3% platinic chloride solution for a few moments, quickly removed, rinsed and dried with absolute alcohol. From the weight after this treatment the residual mass of zinc was calculable, since the absence of hydrogen evolution indicates stoichiometric replacement. Such material was completely soluble in a half hour's time.

In order to insure saturation of the evolved hydrogen with water vapor and prevent entrainment of solution, bulb E was slightly modified. It was made cylindrical, and had a separate thin, slightly convex bottom attached by rubber tubing. Instead of sealing the top, a small rubber stopper carrying a downward extending glass rod was provided. This rod nearly touched the convex bottom, so that when the bottom was broken, the rod pushed out the stopper. The bakelite head G then served as a bubbler for the gas. The zinc was prevented from issuing from the cylindrical part of the container by means of rather coarse mesh screens of fine platinum wire, held in place by tantalum spring-rings.

Five determinations of the heat of solution of the pure zinc metal in acid concentrations similar to Richards and Thorvaldson's were made, of which the two reported in Table III were completely satisfactory. The first three were made upon unplated zinc, where the action of the acid on the zinc was enhanced in the first by mechanical contact with a platinum wire, and in the next two by the addition of small amounts of platinic chloride solution to the acid. In the first case complete solution required more than four hours' time, and in the following two cases three, and one and one-half hours, respectively-. The results obtained were identical with those shown in the table to within *125 calories, but are not reproduced in full because they were obviously not completely satisfactory. Large temperature corrections were involved in this time period, and the uncertainty involved in correcting for the platinic chloride added was considerable. The concordance of ΔC_p values in the two completely satisfactory determinations of Table III is taken to indicate that further experiments would not change the results for the materials used.

From data of the "International Critical Tables" the vapor pressure of water above these solutions at the average temperature of Expt. 6 (24.99°) is estimated to be 20.3 mm., the corrected atmospheric pressure being 760.0 mm., including a small hydrostatic pressure on the exit gas. Then 0.001219 mole of water vapor was carried off by the hydrogen; correcting the heat of vaporization of water, 10,450 calories, for the relative partial molal heat content of water in these solutions, 28 calories, the heat absorbed in vaporization is 127.7 calories, or 287 calories per gram atom of zinc. From this the dissolution of zinc to produce dry gas becomes $\Delta H_{298} = -32,190$, as compared to $-32,654$ calculated from Richards and Thorvaldson, and the heat of formation of zinc oxide from the author's results is then $\Delta H_{298} = -83,208$. This final figure differs by but 50 calories from the results obtained using Richards and Burgess' heat of solution of zinc, and it seems certain that Richards' earlier results were the more accurate. The difference between

TABLE III

SOLUTION OF ZINC METAL, RICHARDS AND THORVALDSON CONCENTRATIONS

	Expt. 6	Expt. 7
Weight of zinc, g.	29.0737	29.9701
Gram atoms of zinc	0.44476	0.45847
Weight of acid, $1HCl:20H_2O$, g	549.17	565.70
Initial heat capacity	5630.2	5658.7
Final heat capacity	5663.3	5692.8
ΔC_p for the reaction	33.1	34.1
ΔC_p per gram atom of zinc	74.4	74.5
Uncorrected temperature rise, °C	2.3971	2.5561
Corrected temperature rise	2.5127	2.5816
Final temperature, °C	26.19	25.63
Heat of the reaction	14147	14608
ΔH at final temperature	−31807	−31862
ΔH_{298} (moist gas)	−31896	−31909

the dissolution of wet and dry oxide as estimated from the blank experiment was shown to be 53 calories, and if this correction be applied to the results of Expts. 1 and 2, which were performed with dry oxide, the heat of formation of wet oxide from these experiments becomes $\Delta H_{298} = -83{,}212$.

The concordance is probably fortuitous, and no accuracy better than 50 calories is claimed.

In the above calculations, the heat of formation of liquid water has been taken from Lewis and Randall as $\Delta H_{298} = -68{,}270$, but Roth has given as a more probable figure $\Delta H_{298} = -68{,}330$.[13] If this latter figure is accepted, the heat of formation of zinc oxide becomes $\Delta H = -83{,}270 \pm 50$.

Conclusion

Except for the work of Parks discussed above, recent thermochemical determinations of the heat of formation of zinc oxide are limited to the experiments of Roth and Chall,[14] who worked at 50°, and obtained results varying from 82,825 to 82,905 calories per formula weight. W. Biltz and Wagner[15] and Biltz and Hohorst[16] determined the heat of solution of metallic zinc in hydrochloric acid, but their results cannot be regarded as significant for the determination of the heat of formation of oxide. By a curiously elliptic process of reasoning, these investigators first determined the water equivalent of their calorimeter by the use of Richards and Burgess' heat of solution of zinc, then gave the heat of solution of zinc obtained from slightly different quantities of metal, differing from Richards by more than 100 calories.

None of the previous investigators seem to have been much at pains to correct their results for the temperature coefficients of the reaction, with the exception of Richards and Burgess and Richards and Thorvaldson. These coefficients are seen from the data given above to be more than 100 calories per formula weight per degree for the solution of oxide, and may result in corrections of several hundred calories in actual cases. In the present work such corrections have been made, as well as those resulting from heats of dilution.

Summary

A calorimeter of some unusual features, including the use of tantalum, bakelite, cooling and heating devices, and a precision resistance thermometer, is described.

The heats of solution of zinc oxide and zinc metal have been redetermined, and the result agree with the earlier work of Richards and Burgess on the metal, rather than the later results of Richards and Thorvaldson.

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[13] Landolt–Börnstein, 5th ed., 1st Ergänzungsband, 1927, p. 829.

[14] Roth and Chall, *Z. Elektrochem.*, 34, 185 (1928).

[15] Biltz and Wagner, *Z. anorg. allgem. Chem.*, 134, 10 (1924).

[16] Biltz and Hohorst, *ibid.*, 121, 16 (1922).

The figure for zinc oxide $\Delta H_{298} = -83{,}270 \pm 50$ (15° calories) is proposed as most acceptable on the basis of experimental work now available. The probable uncertainty of about 50 calories is nearly the same as may be inherent in the heats of formation of water as used. The experimental results confirm estimates by thermodynamic methods.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE ADSORPTION OF WATER AND BENZENE VAPORS BY MANGANESE DIOXIDE[1]

BY H. W. FOOTE AND J. K. DIXON

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Manganese dioxide is an active catalyst for the oxidation of carbon monoxide. Bray and his students[2] have made a very complete investigation of the properties of copper oxide–manganese dioxide catalysts. Bray and Draper[3] have determined water isotherms for these oxide mixtures at 25° and showed how these vapor isotherms could be used in determining the structure of the oxides. Whitesell and Frazer[4] have developed a method for preparing manganese dioxide, yielding a product which is a more active catalyst than the mixtures with other oxides. The present investigation deals with the adsorption of water and benzene by manganese dioxide prepared according to this method. The effects on the adsorption isotherms of temperature, temperature of outgassing, and the presence of permanent gases have been investigated and the results have been used to draw some conclusions with regard to the structure of the oxide and the mechanism of the adsorption process.

Materials

The manganese dioxide used in the adsorption isotherms was prepared by sifting finely powdered C. P. potassium permanganate into concentrated nitric acid, according to the method of Whitesell and Frazer.[4] The suspension was stirred by a motor at a temperature of 25–30°. After complete reaction, the oxide was allowed to settle, then filtered and washed until the filtrate showed no test for nitrates. The product was dried for seventy-two hours at 110–115°. The product was then further washed by decantation and on the filter for a week. Different lots of this material were heated

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[1] An abstract of a dissertation presented by J. K. Dixon to the Graduate School, Yale University, 1929, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Almquist and Bray, THIS JOURNAL, **45**, 2305 (1923); Hoskins and Bray, *ibid.*, **48**, 1454 (1926); Bray and Doss, *ibid.*, **48**, 2060 (1926).

[3] Bray and Draper, *Proc. Nat. Acad. Sci.*, *12*, 295 (1926); Draper, THIS JOURNAL, 50, 2637 (1928).

[4] Whitesell and Frazer, *ibid.*, 45, 2841 (1923).

at the temperatures desired, and were then analyzed. The temperatures and composition of the oxide after heating are given in Table I.[5] Manganese was determined as the pyrophosphate, available oxygen by the oxalate method, water by the Penfield method, and impurities by difference.

TABLE I

TEMPERATURE OF HEATING AND COMPOSITION OF PRODUCT

Temperature of heating, °C. ..	190	390	475
Ratio, O:Mn.	1 93	1 85	1 51[a]
Percentage of H_2O	2 81	1 02	
Percentage of impurities (by difference)	0 32	1 64	

[a] Oxide analyzed after use in a water isotherm

The benzene used had been washed five times with mercury, four times with sulfuric acid, and then recrystallized twice. It was dried over sodium and distilled from this metal directly into the adsorption apparatus. The boiling point of the benzene was 80.04° at 760 mm.[6]

Apparatus and Experimental Procedure

The adsorption isotherms were determined in an apparatus in which the amount of vapor adsorbed was determined by direct weighing It is similar in principle to the apparatus described by Zsigmondy, Bachmann and Stevenson.[7] A diagrammatic sketch is shown in Fig. 1. The apparatus was of pyrex glass and was evacuated by means of a mercury pump which was backed by an oil pump. Pressures above 2 mm were determined with an accuracy of ±0 05 mm by measuring the difference in height of the mercury column at N, by means of a cathetometer. Pressures from 0 001 mm. to 2 mm. were determined by means of a modified McLeod gage, L It consisted of a bulb, D, of known volume, to which was attached the glass tubing, EFGHI. The section of tubing, EF, was of 12 mm. bore, FG was of 6 mm , and GHI was large capillary tubing. The volumes of the tubing and bulb were determined by calibration with mercury and water, respectively. The calibration figures are given in Table II.

TABLE II

CALIBRATION DATA

	Volume, *cc.* per cm	Length, cm.
GH	0 041	12 5
FG	131	40 7
EF	585	24 0

Volume of D (from J to E) = 186 4 cc

The pressure of the vapor after compression was given by the difference in heights of the mercury columns at H and I. Since the volume of vapor before and after com-

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[5] The second long washing noted above was subsequently found to be unnecessary. Two adsorption isotherms carried out with material which had only been subjected to the first washing showed nearly identical but slightly greater adsorption than the more thoroughly washed material.

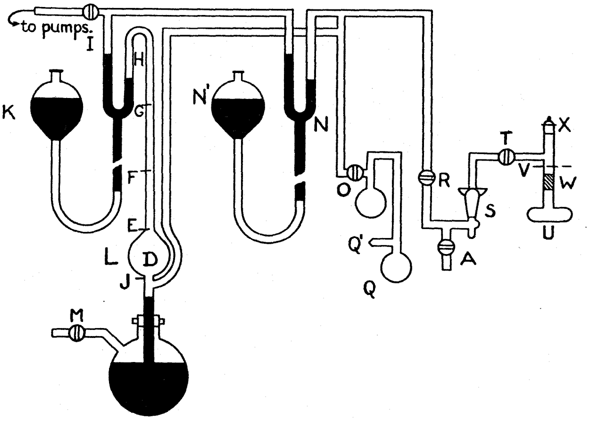
[6] We are indebted to Dr. R. P Smith of this Laboratory for this very pure product and for the boiling point determination

[7] Zsigmondy, Bachmann and Stevenson, *Z anorg* Chem , 75, 189 (1912); Anderson, *Z. physik. Chem.*, 88, 191 (1914)

pression and the final pressure were known, the pressure in the apparatus could be easily calculated. The pressures calculated checked the values found at N when they were of the order of 1–2 mm. and were accurate to 2%. Coolidge[8] has pointed out that such a gage may give erroneous results below 0.01 mm. Our experimental results below this pressure, however, show no peculiar or irregular behavior and indicate that the pressures are correct.

The vapor used in the adsorption isotherms was distilled into Q through Q' in a vacuum produced by opening stopcock O. Distillation between the two bulbs a number of times, with intermittent pumping, served to remove any permanent gases dissolved.

The bulb, U, which contained the manganese dioxide, had a volume of 14.4 cc. X is a ground-glass stopper which was sealed with wax; T, a stopcock; and S, a ground joint. By unseating the bulb at S, after closing T, it was possible to determine the weight of the adsorption bulb with its contents. Ramsay grease was used at S and removed with ether before each weighing of U. Any weighing could be checked within 0.2 mg. after greasing the joint S again and recleaning. A small plug of ignited asbestos at W, weighing less than 0.2 g., prevented the adsorbent from flying out of the bulb when it was heated and outgassed. A preliminary experiment had shown that the vapor adsorbed by the asbestos was negligible.



Pig. 1.

The procedure in determining an isotherm was as follows. The weight of the evacuated adsorption bulb was found and from 3 to 4 g. of manganese dioxide introduced. The asbestos was introduced, the stopper put in place and sealed with wax, and the weight of wax and asbestos determined. By proper manipulation of stopcocks T and R and the leveling bulb, N', the adsorbent was pumped free of gases. A small platinum-wound furnace was drawn up about U and the bulb containing adsorbent was heated at the desired temperature while being subjected to the full vacuum produced by the pumps. The temperature was indicated by a calibrated thermometer clamped against the bulb, U, and could be kept constant within ±3°. After outgassing in this manner, U was cooled and weighed. The actual weight of outgassed oxide could then be calculated.

The bulb, U, was now reseated at S and immersed in the thermostat, the tubing from R to T evacuated and a suitable amount of vapor admitted to the system through

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[8] Coolidge, THIS JOURNAL, 46, 596 (1924).

O. The stopcock, T, was then opened, The oxide adsorbed the vapor until equilibrium was reached, which was shown by a constancy of pressure. The time to reach equilibrium was four hours or longer, depending largely on the temperature. The weight of vapor taken up was found by removing and weighing the bulb, U Each successive point in an adsorption isotherm was determined in a similar way, and it is apparent that either adsorption or desorption curves could be found. The weight of vapor adsorbed was corrected for the amount of vapor as such in the bulb.

Adsorption isotherms at 25 and 40° were obtained by immersing U in a well-stirred water thermostat up to the mark V. Isotherms at 0 and −17.46' were found by immersing the bulb in ice and water, and in the eutectic mixture of ice and sodium nitrate.[9]

Attempts were made to determine corresponding isotherms for carbon tetrachloride and certain alcohols, but they were unsuccessful, due to oxidation by the manganese dioxide.

The Adsorption Isotherms for Water and Benzene

The data for a typical adsorption and desorption isotherm are given in Table III. The first column, p, gives the observed vapor pressure in millimeters of mercury and the second column, p/p_0, is the ratio of the observed vapor pressures to that of pure water at the temperature of the experiment (25°). The third column, q, gives the weight of water adsorbed by one gram of the outgassed oxide.

TABLE III

ADSORPTION AND DESORPTION OF WATER BY MANGANESE DIOXIDE WHICH HAD BEEN OUTGASSED AT 190° (SEE TABLE I). $t = 25°$

p	p/p_0	q	p	p/p_0	q	p	p/p_0	q
0.0276	0 00116	0.0207	17 30	0 728	0 2166	16 20	0.682	0.2297
,137	,00577	.0295	17.60	.741	.2204	14.95	.630	.1885
.308	.0130	.0332	17 65	.743	.2276	14.80	.623	.1726
.903	.0380	.0401	18.50	.779	.2539	14.35	.604	.1538
3.65	.154	.0561	19.15	.806	.2674	13.30	.560	.1302
7.60	.320	.0707	20.70	.871	.2739	10.40	.437	,1027
10.45	.440	.0901	21.60	.909	.2766	6.70	.282	,0851
15.35	.646	.1432	18.70	.787	.2700	3.45	.145	.0737
1600	.674	.1546	17.10	.720	.2592	2.10	.0885	.0668
16.75	.705	.1799	16.50	.695	.2398	1.50	.0633	.0626

The results are plotted in Fig. 2.[10] The broken lines between the two curves are taken from a subsequent experiment and illustrate the way transitions occur from desorption to adsorption curves, or the reverse. Hysteresis is present and, as so often in other cases, seems to be due to some property of the adsorbent. Lambert and Clark[11] observed hysteresis

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[9] "International Critical Tables," Vol. IV, p. 259.

[10] The time allowed for the system to reach equilibrium extended overnight in some cases, but these points show no regular deviation from points determined in the usual way.

[11] Lambert and Clark, Proc Roy. *Soc.* (London), **117A,** 183 (1927); *ibid.*, **122A,** 497 (1929).

in the adsorption of benzene by ferric oxide; with the same apparatus and experimental procedure, they found none in the adsorption of benzene by silica gel. Since each isotherm exhibited hysteresis phenomena exactly similar to that shown in Fig. 2, only the adsorption curves will be considered in the subsequent curves and discussion.

Figure 3 shows the adsorption isotherms of water on the oxide (outgassed at 190°) at the temperatures —17.5, 0, 25 and 40°. Here log q is plotted against log *p*, q and *p* representing, as before, the weight of water adsorbed per gram of oxide, and the corresponding pressure. The isotherms at 25 and 40° are each plots of two separate series of determinations and show that, with a fixed method of treatment, the oxide gives reproducible adsorption curves. The two series at 25° were determined three months apart, showing that the oxide did not change during this time. Also, the water used in the later series had been standing in the apparatus for two months in the absence of air with occasional intermittent pumping, so that the presence of traces of gases from this source is excluded. The adsorption isotherms of benzene on the oxide (outgassed at 190°) were determined at 0 and 25° and the results are shown (together with two other isotherms mentioned later) in Fig. 4.

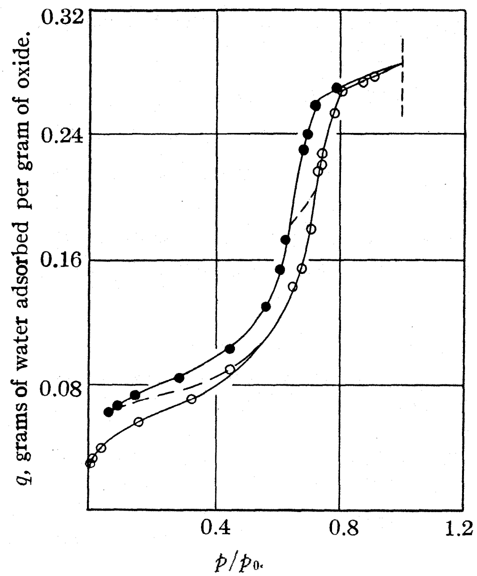

Fig. 2.—Adsorption isotherm for water on manganese dioxide at 25°: o, adsorption; ●, desorption.

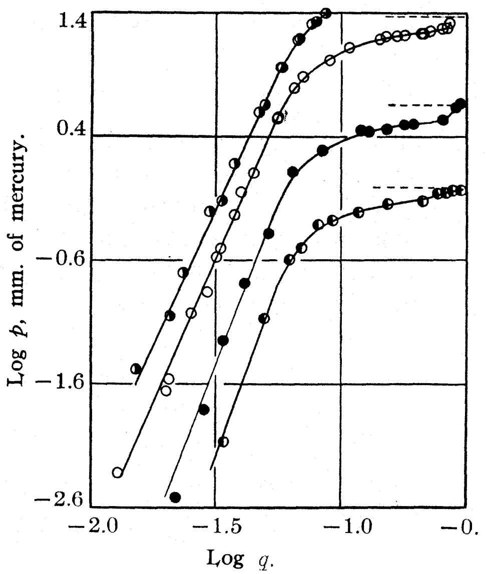

Fig. 3.—Adsorption isotherms for water on manganese dioxide: ◑, 40"; ○, 25°; ●, 0°; ◐, −17.5'.

The isotherms for water and benzene show that these vapors are adsorbed at lower pressures in the same way that permanent gases are adsorbed by charcoal, since the log p–log q curves are nearly straight. It is reasonable to assume that pure surface adsorption is taking place over this range of pressures. At a value of p/p_0 of about 0.5, the isotherms break rather sharply and the amount of vapor adsorbed increases rapidly with a small increase in pressure. If this great increase in the rate of adsorption is due to condensation in the capillary spaces of the oxide,[12] the radii of the capillary spaces can be calculated by means of Thomson's equation.[13] Such calculations for water and benzene at different temperatures give values which are in good agreement, the capillaries having radii extending from 10 to 40 Å. Shereshefsky[14] has shown that for very small capillaries, however, the surface tension of the condensing liquid is not normal, and Polanyi and Goldmann[15] have shown that the density of an adsorbed liquid is greater than that of the free liquid. For these reasons, it is doubtful if calculations by the Thomson equation have more than qualitative significance.

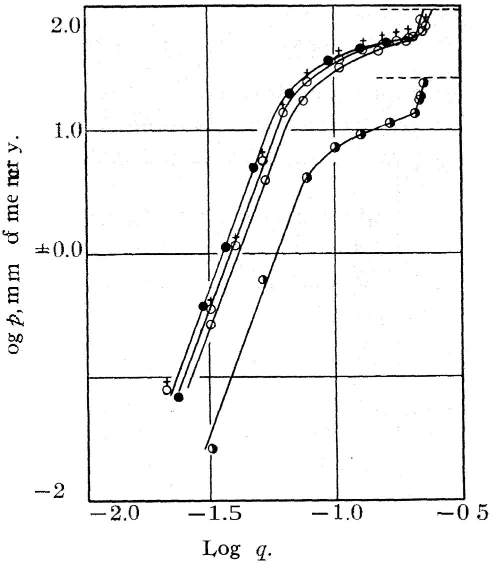

Fig. 4.—Curves showing the adsorption isotherms of benzene on MnO_2: ◑, 0°; ⊙, 25° (oxide outgassed at 190° in both isotherms); ȯ, 25°, oxide outgassed at 290°; ●, 25°, same as last with oxide outgassed two hours more at 190°.

Polanyi has developed[15,16] an expression for the so-called adsorption potential which, so far as it is applicable, can be used to calculate the adsorption isotherms for a given adsorbent and vapor at any temperature when one isotherm is known. Aq, the adsorption potential, is given by the equation: $Aq = RT \ln (p_0/p)$, in which R is the gas constant, T, the absolute temperature and p and p_0 have their usual significance. Plotting Aq against q, the curves should coincide at all temperatures, if correction is made for the change with temperature of the density of the adsorbed vapor. When their results were uncorrected for density changes, Polanyi and Goldmann[15] found experimentally that a lower temperature curve fell above a higher temperature curve in the cases of chloroform, carbon bisulfide, ether and pentane ad-

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[12] Huckel, "Adsorption und Kapillarkondensation," Part III, Leipzig, 1928.

[13] Thomson, *Phil. Mag.*, [4] *42*, 438 (1871)

[14] Shereshefsky, THIS JOURNAL, 50, 2966, 2980 (1928)

[15] Polanyi and Goldmann, Z. *physik. Chem*, *132*, 321 (1928)

[16] See also Lowry and Olmstead, J. *Phys Chem*, *31*, 1601 (1927)

sorbed by charcoal. In Fig. 5 our data for water and benzene, uncorrected for density changes, have been plotted in the same way. The coincidence of the curves, on the whole, is surprisingly close. The curves for water are almost identical except at −17.5° for high values of p/p_0, where the difficulties of accurate determination are great. Polanyi's theory postulates surface adsorption and, subsequently, liquefaction of the adsorbed vapor, which is in accord with the theory of capillary condensation. The two theories differ in that they propose different causes of liquefaction. The theory of Polanyi has proved to be the more useful.

The Effect of the Temperature of Outgassing

Almquist and Bray[17] have shown that the catalytic activity of CuO–MnO_2 mixtures decreased as the temperature of dehydration was increased above 200°. Drucker and Hüttner[18] have shown that when manganese dioxide is heated, it loses oxygen somewhat irreversibly, forming a lower oxide on the outside of the particles. We have investigated the effects of the temperature of outgassing on the adsorption isotherms in order to show the surface and other structural changes taking place on heating.

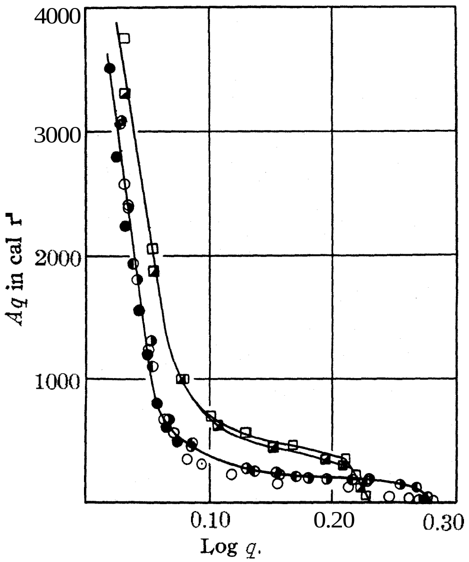

Fig. 5.—Adsorption potential curves for water and benzene on manganese dioxide. Water: o, −17.5"; @, 0°; @, 25°; @, 40°. Benzene: O, 0°; ▨, 25".

For this purpose a sample of manganese dioxide was heated in a vacuum for three hours at 290° and the benzene isotherm at 25° determined. The oxide was then outgassed for two hours more at 190° and the benzene isotherm at 25° again determined. The results are plotted in Fig. 4, together with two isotherms previously mentioned.

Water isotherms at 0° were determined (a) on a sample previously used for a 0° isotherm and which was then heated at 390° for three hours, and (b) on a sample heated at 475° for three hours. These two isotherms, together with one on material heated normally at 190°, are plotted in Fig. 6. The diagrams show that preliminary heating has a marked effect on the adsorption curves only when the temperature is so high (475°) that

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[17] Almquist and Bray, This journal, 45, 2305 (1923).

[18] Drucker and Huttner, *Z. physik. Chem.*, 131, 237 (1928).

the composition of the oxide is materially changed, as shown by Table I. On this high-temperature oxide, both surface adsorption and that attributed to capillary condensation are markedly decreased, due to sintering or to the formation of an inactive lower oxide, or both. When capillary condensation begins on this oxide the capillaries have radii of 54 Å. (using the Thomson equation), which is three times the value found for the oxide outgassed at 190°. The accompanying decrease in surface area will not account for more than one-tenth of the decrease in surface adsorption at low pressures. Hence, the state of the surface as well as its area is important in the adsorption process. The surface adsorption of water vapor is a measure of the ability of the oxide to take up a gas by primary adsorption, and Benton[19] has pointed out that this adsorption is a measure of catalytic activity as far as the oxidation of carbon monoxide is concerned. It is probable that the parts of the vapor isotherms due to capillary condensation yield information only with regard to surface area and uniformity of the capillary spaces and are otherwise useless in predicting catalytic phenomena.

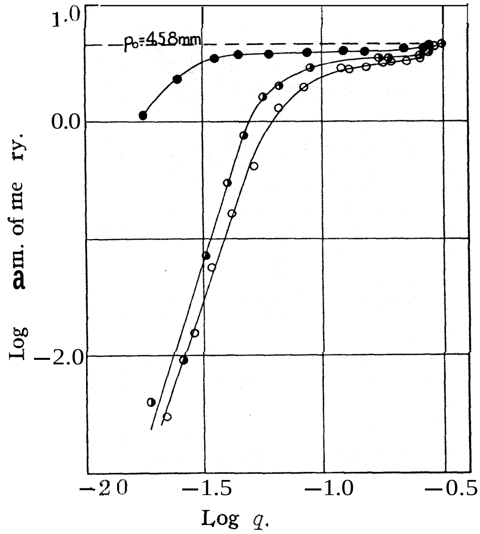

Fig. 6—Curves showing the effect of the temperature of outgassing on the water isotherms for MnO_2 at 0°. Temperature of outgassing: ○, 190°; ◐, 390°; ●, 475°.

The oxide outgassed at 475° corresponds closely to Mn_2O_3. Its water isotherm showed very little hysteresis, and for this reason it is probable that the manganese dioxide is the cause of any difference between the adsorption and desorption curves of an isotherm, rather than traces of any gas. If, for instance, adsorbed oxygen coats the oxide particles and causes hysteresis at lower outgassing temperatures, there appears to be no reason why it should not do so when the outgassing temperature is increased, with correspondingly increased oxygen pressure.

The Effect of the Presence of Permanent Gases

If a permanent gas is adsorbed on the surface of the manganese dioxide, it should cover the most active adsorbing patches and reduce the area available for the surface adsorption of a vapor. Capillary condensation (or condensation caused by forces acting between adsorbent and vapor)

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[19] Benton, THIS JOURNAL, 45, 887, 900 (1923).

should be little affected by the presence of permanent gases. This was found to be the case experimentally. The effects of adsorbed carbon monoxide and carbon dioxide were entirely similar to each other, so the results for the former will be given as typical of both.

Experiment 1.—Carbon monoxide, which had been dried carefully by passing through sulfuric acid and phosphorus pentoxide, was admitted to a sample of manganese dioxide which had been outgassed as usual at 190° for three hours. The equilibrium pressure of the gas after adsorption was 29.6 mm. The gas was then removed by pumping for one hour and the water isotherm at 25° determined.

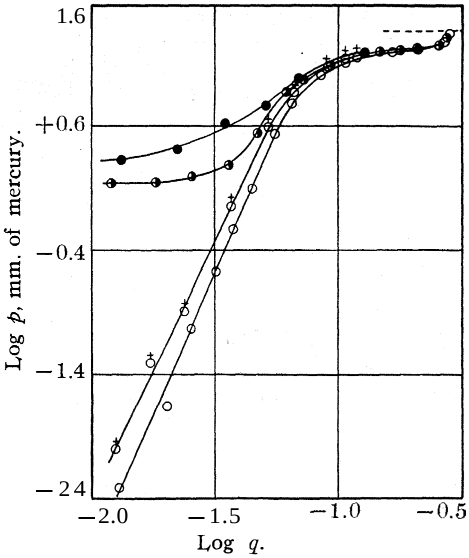

Fig. 7.—Curves showing the effect of the presence of carbon monoxide on the water isotherms for MnO_2 at 25°: o, carbon monoxide absent; @, carbon monoxide present; @, carbon monoxide present (greater amount); ♁, same, after outgassing at 190°.

Experiment 2.—Similar to Experiment 1; equilibrium pressure of carbon monoxide 88.5 mm. The gas was removed by pumping for one and one-half hours; pressure after standing for twelve hours, 0.215 mm. The gas was again pumped off for one hour, and the water isotherm determined as before. The oxide was then outgassed at 190° and the water isotherm redetermined. The results of the three isotherms are plotted in Fig. 7. It is evident that surface adsorption has been markedly reduced, the effect being greater at lower pressures. There is no effect on that portion of the water isotherm attributed to capillary condensation. Very possibly the water displaced some of the permanent gas from the surface, which would mean that the pressure of the water vapor was less than that measured, but this would merely decrease the difference between a treated and untreated oxide. This error would be negligible at pressures where condensation begins. The experiments with oxygen were carried out similarly.

Experiment 3.—(Run in duplicate.) After outgassing the oxide, dry oxygen was admitted at a pressure of 135 mm. There was no evidence of adsorption. After evacuating and allowing the apparatus to stand for twelve hours, the pressure was less than 10^{-4} mm. The water isotherm was then determined as before at 25°. This was identical, within the errors of the experiment, with an isotherm run on the outgassed oxide, which had not been treated with oxygen, and the hysteresis had not been changed.

These experiments with the three gases show rather definitely that the vapor isotherms run on the outgassed oxide have been measured on an oxide surface and not on a surface covered with oxygen. Carbon monoxide and carbon dioxide cover the active adsorption patches, reducing the surface adsorption of water, while oxygen has no effect. Condensation of water on the adsorbent (which occurs at the higher pressures) is not measurably affected by the permanent gases. Heating removes the permanent gas which is adsorbed, cleaning up the surface of the oxide, and restores the surface adsorption of water vapor to its normal value.

Summary

The adsorption isotherms of water on manganese dioxide have been determined at −17.3, 0, 25 and 40°, and corresponding isotherms for benzene at 0 and 25°. The isotherms consist of two parts due to surface adsorption and condensation of the vapor on the surface of the oxide. Polanyi's theory of adsorption is in agreement with the data.

When the temperature of outgassing is raised, the surface adsorption for water is greatly reduced, due to the destruction of active adsorption patches. The treatment of the oxide with a permanent gas which can be adsorbed reduces the surface adsorption of water vapor and leaves the part of the isotherm due to condensation unaltered. The use of vapor isotherms in predicting the catalytic behavior of an oxide has been discussed.

The isotherms exhibit hysteresis and the present experiments indicate that this phenomenon is not due to false equilibrium or the presence of permanent gases on the surface of the oxide.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, UNIVERSITY COLLEGE OF SCIENCE]

MEASUREMENTS OF THE ELECTROMOTIVE FORCE OF THE CALOMEL ELECTRODE AGAINST THE HYDROGEN ELECTRODE AT LOW CONCENTRATIONS OF HYDROCHLORIC ACID

BY JNANDRANATH MUKHERJEE AND KALI KUMAR KUMAR

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Introduction

It is well known that the calomel electrode is not reliable at concentrations of hydrochloric acid below 0.03 N.[1] There is a difference of opinion as to the causes responsible for the unreliability of calomel electrodes.[2] Our observations generally corroborate previous authors and deal with the questions (a) how far the observed potential can be taken as a measure of the actual concentration of the hydrochloric acid in the cell, and (b) the nature of the chemical reactions responsible for the observed change in concentration.

Experimental

The chemicals used were Merck's "Reagent" or Kahlbaum's "pro analyse" quality purified as usual. The hydrogen was obtained from electrolysis of a strong solution of

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[1] Ellis, THIS JOURNAL, 38, 737 (1916); Noyes and Ellis, ibid., 39, 2532 (1917).

[2] See Clark, "Determination of Hydrogen Ions," The Williams and Wilkins Co., Baltimore, 3rd ed., 1928, p. 309.

caustic potash. Dolezalek type hydrogen electrodes, prepared from borosilicate glass, having ground-glass joints were used. The type of calomel cell was a simplified form of that given by Clark.[3] Our measurements relate to the e. m. f. of the system $\mathrm{Hg}-\mathrm{HgCl}/\mathrm{HCl}(C_1)/\mathrm{HCl}(C_2)/\mathrm{HCl}(C_2)/(\mathrm{Pt})\mathrm{H}_2$. A set of three to four calomel electrodes was set up against a hydrogen electrode. A tall cylinder filled with acid of approximately the same concentration was interposed between the two electrode vessels. The side tubes of the electrodes dipping into the cylinder were kept plugged except when measurements were taken. The thermostat was kept at 35 * 0.1'. A Leeds and Northrup K type potentiometer (bridge wire calibrated in the laboratory) was used. The galvanometer used was very sensitive up to 0.01 *N* hydrochloric acid but not so with more dilute solutions. The hydrogen electrode vessels after cleansing with conductivity water were rinsed several times with the solution in which the electrode was completely immersed. Hydrogen was passed into the vessel for two hours, at first keeping it at room temperature. The electrode vessel was then removed to the thermostat and the stream of hydrogen was continued for about two hours more, though one hour was found to be sufficient for attainment of equilibrium.

Calomel Electrode.—The paste was prepared by gently shaking for half an hour the hydrochloric acid solution with about 1 cc. of mercury and 5 to 8 g. of calomel powder in a 100-cc. (wide mouth) stoppered bottle. The bottle was then kept in a thermostat for about two days. Jena glass vessels were used for dilute solutions less than 0.05 N. The supernatant solution was then removed and titrated against standard baryta with phenol red as indicator and the change in concentration was noted. The bottle was then refilled with acid solution previously saturated with calomel and the whole procedure repeated. Both the calomel electrode vessel and the cylinder interposed between it and the hydrogen electrode were kept in the thermostat for two days before the e. m. f. was measured.

A. The Observed E. m. f. and the Concentration of the Acid.—On passing hydrogen gas for a long time, the concentration of acid increased slightly and to avoid this the e. m. f. within an hour after attainment of a steady value was noted. An appreciable fall of the concentration of the acid in the calomel electrode vessel was observed even in 0.05 N solution. It will be seen from Table I that the concentration was found to correspond approximately to the observed e. m. f. In the case of the more dilute solutions the change in concentration was considerable and a correction (Nernst's formula has been used) for the liquid junction potential resulting therefrom was felt necessary. The activity coefficients as generally given in the literature refer either to the freezing point or to 25°. The present measurements were made at 35° at which temperature Ellis[1] gives a value of 81.4 for 0.1 N. The values given by Lewis and Randall[4] have been found to disagree with the results of very careful measurements of Randall and co-workers.[4,5] For a proper extrapolation it is necessary to know the heats of dilution at different temperatures. The heat capacities[6] have been given

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[3] Ref. 2, p. 304B.

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 362.

[5] Randall and Vanselow, THIS JOURNAL, 46, 2434 (1924).

[6] Lewis and Randall, Ref. 4, p. 279.

by Randall and Ramage,[7] but the recent determinations of these quantities by Randall and Rossini have not yet been published.[8] An examination of the activity coefficients given by Randall and Young[g] shows that at 0.1 N the activity coefficients at the freezing point and at 25° are, respectively, 80.22 and 79.56, a difference of 0.66. This difference will evidently be smaller at the lower concentrations. By extrapolation the value for the activity coefficient at 25° for 0.1055 N is found to be 79.26. We have taken the value 79.0 for 35°. The existence of the liquid junction potential makes such an approximation permissible and high accuracy is not claimed. In Table I are given C_1, the concentration of the acid in the calomel vessel (as determined after the measurement of the e. m. f.); C_2, the concentration in the hydrogen electrode; the observed e. m. f. ($E_{\text{obs.}}$); E_l, the liquid junction potential calculated as above; E_x, the magnitude only of the e. m. f. which corresponds to the difference in e. m. f. at either electrode if the concentration of the acid around it had the same value as that in the other electrode and assuming that the activity coefficient is the same for the concentrations in the two electrode vessels; E_{c_1}, the e. m. f. of the cell (Pt) $H_2/HCl(C_1)/HgCl–Hg$ is given by $E_{\text{obs.}} - E_l + E_x$; E_{c_2}, the e. m. f. of the cell (Pt) $H_2/HCl(C_2)/HgCl–Hg$ is given by $E_{\text{obs}} - E_l - E_x$; γ in Table II denotes the percentage activity coefficients of the acid calculated as above. The value of N,, the transport number of hydrogen ions at 35°, has been taken to be 0.815.[10]

TABLE I

EXPERIMENTAL DATA

	c_1	c_2	$E_{\text{obs.}}$	E_l	E_x	E_{c_1}	E_{c_2}
1	0.1085	0.1085	0.3957	0	0	...	...
2	.0555	.0555	.4290	0	0	...	...
3	.0209	.02508	.4771	0.0030	0.0048	0.4789	0.4693
4	.0162	.0172	.4911	.001	.00157	.4917	.4886
5	.0112	.0126	,5085	.0019	.0031	.5097	.5035
6	.0102	.0113	.5114	Annulled (Saturated KCl	.0027	.5141	.5087
7	.00365	.00403	.5645		.0026	.5671	.5619
8	.00343	.00403	.5667		.0042	.5709	.5625

Sometimes at the lower concentrations the titer of the acid in the electrode vessel was found to have decreased by as much as 20% after the e. m. f. measurement. At the last three concentrations, instead of calculating the liquid junction potential, a saturated solution of potassium chloride was inserted. The activity coefficients given in Table II show, in view of the uncertainty as to the liquid junction potential, that the change in the concentration of the acid is mostly responsible for the observed unreliability

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[7] Randall and Ramage, THIS JOURNAL, **49**, 93 (1927).

[8] See Randall and Young, *ibid.*, p. 996, footnote (a).

[9] Ref. 8, p. 995.

[10] Landolt–Börnstein, "Tabellen," **1911**, pp. 1122,1124.

TABLE II

CALCULATED ACTIVITY COEFPICIENTS

Concn.	0 1085	0 0555	0 02508	0 0209	0 0172	0 0162
γ (obs.)	(79)	82 5	84 7	85 7	86 6	86 7
γ (R. and Y. at 25° by interpolation)	7926	824	86.4	873	88.1	884
Concn.	0 0126	0.0113	0 0102	0 00403	0.00365	0.00343
γ (obs.)	88 7	88 8	90.7	92.3	92 3	90.7 (?)
γ (R. and Y. at 25° by interpolation)	896	900	904	93.5	938	93.9

of the calomel electrode, and that the slight trace of mercuric chloride which may be assumed to be present has little effect. The influence of such factors as grain size, surface structure, or incomplete equilibrium between the different regions of the system suggested by previous workers[2] is of minor importance. The procedure used had, however, the effect of minimizing their influence.

B. The Chemical Reactions Responsible for the Observed Change in Concentrations.—The progressive diminution of the concentration of the acid in a mixture containing calomel and mercury is illustrated in Table III. On introduction of electrolytic oxygen, the rate increases markedly, while on expulsion of the dissolved oxygen the reaction practically ceases, in conformity with the experience of others.

In a 500-cc. Jena glass-stoppered bottle about 300 cc. of 0.0108 N hydrochloric acid solution was taken and 13.5 g. of mercury and 5 g. of mercurous chloride were added. The bottle was made air-tight with a coating of paraffin, shaken for an hour and kept in the thermostat. A measured volume of the supernatant liquid was withdrawn at different intervals and titrated against a standard solution of baryta (0.0176 N). The bottle was made air-tight after each withdrawal of the liquid. The decrease in acid concentration has been given as percentage of the original.

TABLE III

DIMINUTION OF ACID CONCENTRATION

Days	1	2	3	4	5	8	9	12	26
Decrease, %	1.3	6.6	7 2	12.0	20.0	22.8	25.0	41 0	58.8

On the ninth day the solution (about 200 cc.) was saturated with electrolytic oxygen, shaken and kept in the thermostat.

The possible chemical reactions[11] are: (a) the oxidizing action of the dissolved oxygen and the action of the liberated chlorine (or of hypochlorous acid formed). No evidence could be obtained of this direct oxidation with starch iodide. (b) Interaction of acid and mercury in presence of oxygen. Calomel is known to be formed from mercury and a solution of potassium

[11] See Mellor, "A Comprehensive Treatise on Inorganic Chemistry," Vol. IV.

chloride in the presence of dissolved air. We have confirmed this and reaction (b). Using 50 cc. of 0.01 *N* potassium chloride and 13 g. of mercury in a Jena glass bottle, a PH of 7.4 developed in eight days and simultaneously a gray deposit of calomel became visible. With 50 cc. of 0.01 *N* hydrochloric acid, a 2% decrease was observed in ninety days, but no reaction for mercuric ions with hydrogen sulfide was obtained in this case or in that of the e. m. f. measurement. The above measurements were repeated at room temperature after driving off the oxygen by boiling, followed by passage of hydrogen at room temperature and then boiling once more. No sign of formation of calomel nor any change in concentration could be observed.

(c) Mercurous chloride may react directly with oxygen. Mercurous chloride, in contact with the acid and air for a week, shows no change in the concentration of the acid. Pure oxygen, however, reacts more quickly with calomel, and mercuric ions can be detected by hydrogen sulfide.

The main reaction thus appears to be (b) above. A mixture of calomel and mercury, however, reacts more rapidly than mercury alone, possibly owing to the formation of mercuric chloride (from the oxychloride in presence of the acid), which disappears as mercurous chloride. Mercurous chloride may also have a direct effect on the velocity of the reaction.

The following experiments (Table IV) show the erratic variations of the concentration when the supernatant solutions are replenished. Four bottles of ordinary glass, each containing 13 g. of mercury, 5 g. of calomel and 50 cc. of 0.024 N hydrochloric acid were kept as usual in the thermostat; 25 cc. of the acid required 25.8 cc. of standard baryta. In each case, after the supernatant liquid had been withdrawn for titration, as much of it as possible was decanted without disturbing the paste and 50 cc. of the original solution was again added. The days are counted since the acid was first added to the bottle.

TABLE IV

VARIATIONS OF CONCENTRATION

No. of bottle	Interval 4th day Titer	4th day % change in concn.	7th day Titer	7th day % change in concn.	10th day Titer	10th day % change in concn.
I	23.6	8.5	23.2	10.0	23.2	10.0
II	23.2	10.8	22.0	14.9	22.6	12.4
III	23.4	9.3	21.9	15.1	20.5	20.5
IV	25.0	3.0	24.7	4.2	22.0	14.8

No. of bottle	12th day Titer	12th day % change in concn	14th day Titer	14th day % change in concn.	16th day Titer	16th day % change in concn	42d day Titer	42d day % change in concn
I	23.5	8.9	24.5	5.0	24.8	3.9	22.5	12.7
II	22.3	13.5	24.4	5.4	24.0	7.0	19.2	25.5
III	23.0	10.8	22.5	12.7	24.1	6.6	22.4	13.1
IV	24.4	5.4	24.8	3.9	24.9	3.5	20.0	22.4

Summary

To summarize, we find (a) that although presence of oxygen and mercury are both essential, mercurous chloride plays an important part in the reaction leading to the formation of calomel and loss of hydrochloric acid and (b) that the observed e. m. f. corresponds within the limits of experimental error, to the actual concentration of the acid in the electrode vessel.

92, UPPER CIRCULAR ROAD
CALCUTTA, INDIA

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF MCGILL UNIVERSITY]

HYDROGEN DISULFIDE

BY K. H. BUTLER AND O. MAASS

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Although hydrogen persulfide was discovered in 1777 by Scheele,[1] it has not proved an attractive subject for investigation and advances in the knowledge of the substance have been made slowly. Sabatier[2] succeeded in distilling the liquid in vacuo. This line of attack was followed by Block and Höhn,[3] who showed that crude hydrogen persulfide gave on fractionation two compounds, H_2S_2 and H_2S_3. Walton and Parsons[4] repeated and extended this work, using quartz apparatus in part.

In the present work the optimum conditions for the preparation of hydrogen disulfide were investigated, a method of purification was developed and the physical properties of the pure substance were determined.

Preliminary Experiments.—Preliminary experiments, which followed closely the final procedure, dealt with the effect of varying composition of the sodium polysulfide on the yields of the products. The results are given in Table I.

TABLE I

EFFECT OF COMPOSITION OF REACTANTS ON YIELD OF PRODUCTS

Polysulfide	Dilution[a]	Crude oil, g. per 100 g. total S	H_2S_3 G. per 100 g. crude oil	H_2S_2
Na_2S_2	750	47	29.0	7.8
$Na_2S_{2.25}$	700	60	21.9	9.3
$Na_2S_{2.50}$	700	59	23.6	13.5
Na_2S_3	650	81	28.6	5.6
Na_2S_4	600	80	25.5	5.6

[a] Dilution indicates weight of solution per gram mole of sodium polysulfide.

The crude oils obtained from the different solutions varied considerably in appearance and properties. The crude persulfide from Na_2S_2 was a

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[1] "Chemische Abhandlung von der Luft und dem Feuer," p. 162.

[2] Sabatier, *Bull. soc. chim.*, [2] 44, 169 (1885).

[3] Block and Hohn, *Ber.*, 41,1961 (1908).

[4] Walton and Parsons, THIS JOURNAL, 43, 2539 (1921).

rather mobile liquid, light yellow in color, and sensitive to impurities. It had *a* very sharp odor and the vapor was highly irritating to the nose and eyes. On fractionation it distilled very readily at 120°.

As the amount of sulfur in the sodium polysulfide solution increased, there was a gradual change in the properties of the resulting persulfide. That obtained from Na_2S_4 was a dark yellow viscous liquid with only a slight odor. It was comparatively stable. The oil distilled very slowly at 120°.

Preparation of Sodium Polysulfide.—These preliminary experiments showed that $Na_2S_{2.50}$ was the most satisfactory polysulfide. It was used in all later preparations of hydrogen disulfide. The solution used was made by heating on a water-bath a mixture containing 150 g. of flowers of sulfur, 725 g. of sodium sulfide crystals and 500 cc. of distilled water. A tared 2-liter flask was used and the mouth closed by a rubber stopper bearing a Bunsen valve. After solution of the solids was complete, distilled water was added to make the total weight of the solution 2650 g. and the flask was tightly stoppered.

Preparation of Crude Hydrogen Persulfide.—The preparation of hydrogen persulfide was carried out in a 3-liter pyrex beaker supported on rubber stoppers within an insulated battery jar used as a cooling bath. A suitable quantity of acetone was introduced into the battery jar and cooled to −40° by the addition of solid carbon dioxide. The pyrex beaker containing 1500 cc. of c. p. hydrochloric acid (sp. gr. 1.19) was put into position and stirring commenced. When the acid had cooled to −15° the sodium polysulfide solution was added from a dropping funnel, the tip of which was immersed in the acid to a depth of *2* cm. During the remainder of the operation the acetone bath was kept below −25° and the flow of the polysulfide solution regulated to keep the acid temperature between −10 and −15°.

After a liter of the solution had been added, the hydrogen persulfide began to rise to the surface as a scum and decompose with evolution of hydrogen sulfide. The addition of sodium polysulfide was then stopped, the beaker replaced by one containing a fresh portion of hydrochloric acid, and the operation completed with the remaining half of the polysulfide solution.

This preparation resulted in an emulsion of crude hydrogen persulfide with suspended sulfur, in an acid solution of sodium chloride. The mixture was allowed to stand for two to three hours with occasional stirring, the yellow crude oil settling mainly to the bottom of the beaker and the finely divided sulfur forming a thick layer just above this. The upper layer of liquid was decanted, the mixture diluted with cold water to one liter, transferred to a separating funnel and the persulfide layer drawn off into a tared Erlenmeyer flask. After the weight of the persulfide had been determined, a few grams of phosphorus pentoxide was added cautiously and the flask allowed to stand overnight. The phosphorus pentoxide was removed by filtering through asbestos and the filtered oil was fractionated. All apparatus used in this preparation was of pyrex and the surface was carefully acidified immediately before use by treatment with concentrated hydrochloric acid.

Fractionation of Hydrogen Persulfide.—The apparatus used in fractionation is shown in Fig. 1. It was built from pyrex glass: A, a 100-cc. flask; B, a special flask made from a 50-cc. distilling flask; C, made from a 100-cc. flask; G, a capillary contraction in the connecting tube. The inner tube of the condenser was constructed of tubing of 9 mm. outside diameter; all other tubing was 5 mm. outside diameter.

Before setting up, all parts of the apparatus were carefully cleaned and dried. The rubber stoppers were soaked in hot beeswax. After setting up, the apparatus was warmed in a current of dry air. Dry hydrogen chloride was then passed through for ten minutes, care being taken to fill the funnel F by displacement. The apparatus was then pumped out using an efficient water pump which reduced the pressure to 10 mm. or less. The flask B was immersed in a bath of glycoline held at 120°. The test-tube D was immersed in acetone at −40°.

To start the distillation, stopcock S was closed, S_2 being open, and the crude hydrogen persulfide was allowed to drop slowly from F. After twenty minutes the flow of persulfide was cut off, though the distillation was allowed to continue for five minutes. The flask B was then one-third filled with a dark reddish-yellow viscous fluid. This was removed by opening stopcock S_2 and closing S, thus drawing the residue into A, where it solidified to a lemon-yellow, semi-crystalline mass. The distillation was then continued as before.

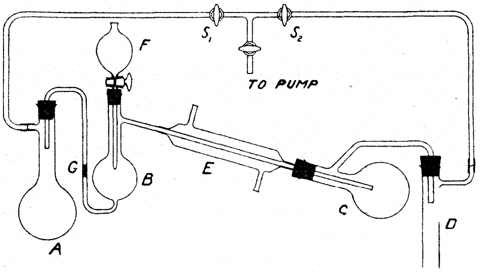

Fig. 1.

Two fractions were condensed. The first, collected in C, was approximately H_2S_3 by analysis and was considered to be hydrogen trisulfide. The second, condensed in D, was H_2S_2, hydrogen disulfide. The two liquids were removed, weighed and placed in quartz bulbs for storage at −78°.

Series of experiments were carried out to determine the effect of temperature and pressure of distillation on the yields of the two products. These results are shown in Table II.

TABLE II

EFFECT OF TEMPERATURE AND PRESSURE OF DISTILLATION ON YIELDS OF DISULFIDE

Sodium polysulfide	Press., mm.	Temp., °C.	G. per 100 g. of crude persulfide Trisulfide	Disulfide
Na_2S_2	10	102	30.2	10.3
Na_2S_2	10	118	29.0	7.8
$Na_2S_{2.50}$	10	112	26.6	15.2
$Na_2S_{2.50}$	10	122	36.5	11.2
$Na_2S_{2.50}$	10	135	14.6	8.3
$Na_2S_{2.50}$	30	120	9.5	10.4
$Na_2S_{2.50}$	18	120	30.3	12.5
$Na_2S_{2.50}$	10	120	36.5	11.3

It is evident that decrease in temperature of distillation leads to increased yields of hydrogen disulfide. The rate of distillation is, however, much slower. The most suitable temperature for the persulfide from $Na_2S_{2.50}$ is 122°. Increase in pressure leads to greatly decreased yields of hydrogen trisulfide.

Cracking of Trisulfide.—Observations were made by Block and Hohn and by Walton and Parsons to the effect that distillation of hydrogen trisulfide gave considerable amounts of hydrogen disulfide as a by-product. This appeared to offer a second method of obtaining the disulfide.

A 100-cc. flask was provided with a 50-cm. reflux condenser and two receivers in series, as in the fractionation apparatus. In one experiment 38 g. of trisulfide was placed in the flask, which was heated to 75° at the start and to 125° at the end. Seventeen g. of hydrogen disulfide was obtained.

Attempts to purify the trisulfide by distillation in vacuo met with slight success. The distillation must be carried out at very low pressures and below room temperature to avoid decomposition.

Purification of Disulfide.—The hydrogen disulfide prepared by the methods outlined above was purified by a distillation in *vacuo* from phosphorus pentoxide.

A pyrex still was used at first and the liquid was transferred by pouring. This type of still gave satisfactory results but the distilled liquid was hygroscopic and owing to moisture picked up in transfer it became turbid on cooling. Trouble was also caused by decomposition when the glass was not thoroughly acidified by the hydrogen chloride passed into the still.

A quartz still was developed in which the hydrogen disulfide was distilled directly into apparatus in which measurements were made and sealed off. This is shown in Fig. 2. A is a 100-cc. distilling flask; the neck and side arm were drawn down and 7-mm. tubing sealed on B is a receiver made from 16-mm. tubing The tube at E is joined to the vacuum line by a de Khotinsky joint. After setting up and drying, phosphorus pentoxide was distilled into A. The air was displaced by dry carbon dioxide and the impure hydrogen disulfide introduced. The tube D was sealed off; the atmosphere of carbon dioxide prevented ignition of the disulfide vapor even at the high temperature needed to work quartz.

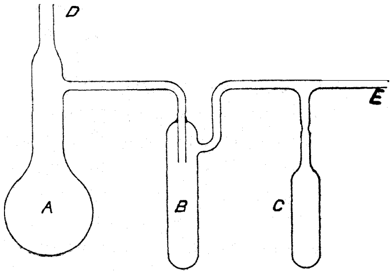

Fig. 2.

The distillation was carried out at 10 mm., A being at room temperature and B at −78°. When the receiver was filled, A was also cooled and the connecting tube sealed. The pressure was then reduced to less than 1 mm. by a Toepler pump and the stopcock to the vacuum line closed. The disulfide was distilled from B to the piece of apparatus attached at C. This was then sealed off.

Method of Analysis.—All analyses were made by the method of Walton and Parsons.[4] A sample of about 1 cc. was transferred to a quartz weighing tube and weighed. The sample was poured into a porcelain evaporating dish and the tube washed with 10 cc. of carbon disulfide. Ten cc. of acetone was added, causing a quiet decomposition of the hydrogen persulfide, The solvents were allowed to evaporate overnight and the sulfur was weighed.

Owing to the small quantities of material available, analyses were made only to check improvements in procedure. The mean results are

	H_2S, %
Crude persulfide from Na_2S_2	17.7
Disulfide from fractionation	47.0
Disulfide from cracking	48 0
Redistilled disulfide	51.3
Theoretical value for disulfide	51.2
Trisulfide from fractionation	32.4
Trisulfide from cracking	32.4
Theoretical value for trisulfide	34.7

Containers for Persulfides.—The problem of keeping hydrogen disulfide and trisulfide presented a number of difficulties. The products from the initial fractionation decomposed rapidly at room temperature, even in all-quartz containers. Long-necked quartz bulbs immersed in solid carbon dioxide were satisfactory for short periods. It was possible to keep the carefully purified disulfide in sealed bulbs for indefinite periods without decomposition.

Cleaning of Apparatus.—The necessity for most rigorous care in cleaning and acidification of all apparatus cannot be too greatly emphasized. Aqua regia proved very useful in cleaning, as an unusually rapid evolution of chlorine indicated the presence of surface impurities. Acidification of apparatus with dry hydrogen chloride was found to be necessary in all cases.

Melting Point.—Two determinations were made of the melting point of hydrogen disulfide. The sample was enclosed in a sealed tube which was immersed in an ether-bath cooled by liquid air.[5] The temperature was determined by a platinum resistance thermometer. The first sample had stood in pyrex glass for eight days at −78"; its melting point was −88.6°. The second sample was condensed in quartz; its melting point was −89.8'.

Freezing Point Curve **with Sulfur.**—The freezing points of solutions of sulfur in hydrogen disulfide were determined in the following way. A quantity of hydrogen disulfide was placed in a small quartz tube and weighed. A suitable quantity of sulfur was added and the tube immersed in a bath of ether cooled by liquid air. The bath temperature was lowered until a solid was precipitated from the solution on stirring vigorously. The temperature was measured by a thermometer in contact with the freezing point tube. This freezing point was then checked, the temperature being varied more slowly. The tube was then removed from the bath, another portion of sulfur added and the mixture stirred until solution was complete. The next point was then obtained. Solution of the solid, which appeared to be sulfur, was very slow unless

TABLE III

FREEZING POINTS OF SOLUTION OR SULFUR IN HYDROGEN DISULFIDE

Run 1, weight of H_2S_2, 1.831 g.

Sulfur added, g	S (added) H_2S_x	Freezing point, °C.
0.020	0 011	−91
.108	055	−55
.156	.079	−41
.240	.116	−23
300	.141	−17
356	.163	−10
.504	.216	− 1
.596	.246	4
.689	.271	7 5
786	300	11 7
.885	.326	13 5
1 003	.354	20.1
1.045	.363	21.0
1.115	.378	22 7

A pentane thermometer was used up to 4° and stem corrections were estimated within 2°.

Run 2, weight of H_2S_2, 1.7035 g.

Sulfur added, g	S (added) H_2S_x	Freezing point, °C.
0.126	0 069	−46
.271	.137	−13 6
.450	.209	− 0 9
562	248	6 3
.744	.303	15 6
.771	.312	17.6
.811	.323	19.4
.897	.345	22 7

A pentane thermometer was used for the first point, and a mercury thermometer for the others.

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[5] Maass and McIntosh, THIS JOURNAL, 36, 738 (1914).

the tube was warmed nearly to room temperature. The results are tabulated and are shown in Fig. 3.

The results obtained by Walton and Whitford are also shown in the figure. These investigators determined the solubility of sulfur in the hydrogen persulfide. They added an excess of sulfur to a sample of the persulfide kept in a constant temperature bath. The mixture was stirred until the equilibrium was reached and a sample of the liquid phase analyzed. They claimed that the disulfide and the trisulfide gave solutions of the same composition when saturated at 0°. Hydrogen trisulfide was used for all points except that at −34.72°, where hydrogen disulfide was substituted. Their results were recalculated to the basis used in the present work.

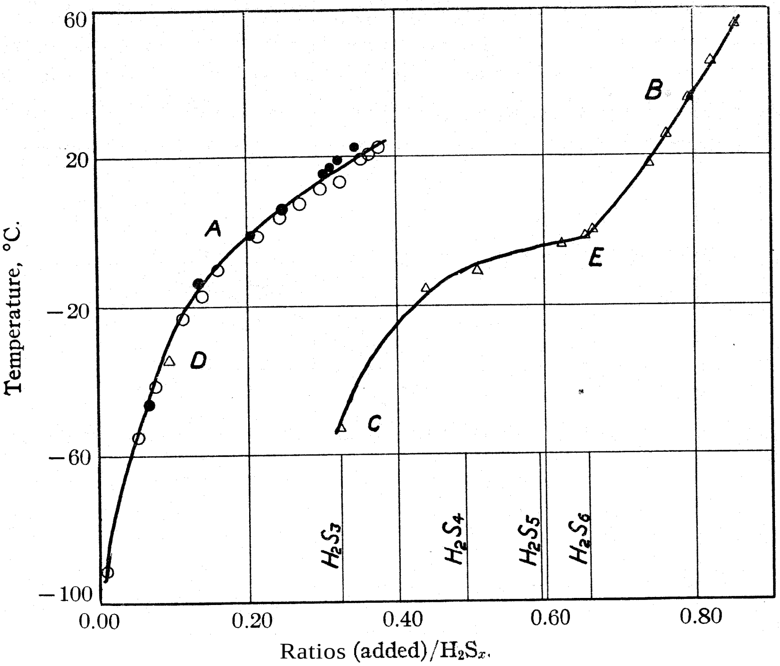

Fig. 3.

TABLE IV

RESULTS OF WALTON AND WHITFORD

Temp., °C.	Sulfur not evolved as H_2S, %	$\frac{(X - 2)S}{H_2S_x}$	Temp., °C.	Sulfur not evolved as H_2S, %	$\frac{(X - 2)S}{H_2S_x}$
−34.72	53.56	0.099	17.92	86.77	0.743
−15.42	71.18	.441	25.4	87.98	.767
−10.6	75.16	.511	35.4	89.46	.795
− 3.75	80.71	.626	45.15	91.00	.825
− 1.45	82.50	.660	55.3	92.49	.854
0.05	82.97	.669			

The ratios corresponding to the various possible persulfides are shown by vertical lines in the figure.

Point C is the freezing point of hydrogen trisulfide as given by Walton and Parsons and by Bloch and Hohn. Point D was obtained by Walton and Whitford using hydrogen disulfide.

Curve **A** represents the solubility of sulfur in hydrogen disulfide. There is no evidence for a break corresponding to the composition $H_2S_2 + S$, and the freezing point of such a solution is far above the recorded freezing point of H_2S_3. It may be stated, therefore, that hydrogen trisulfide is not a molecular compound of hydrogen disulfide with sulfur.

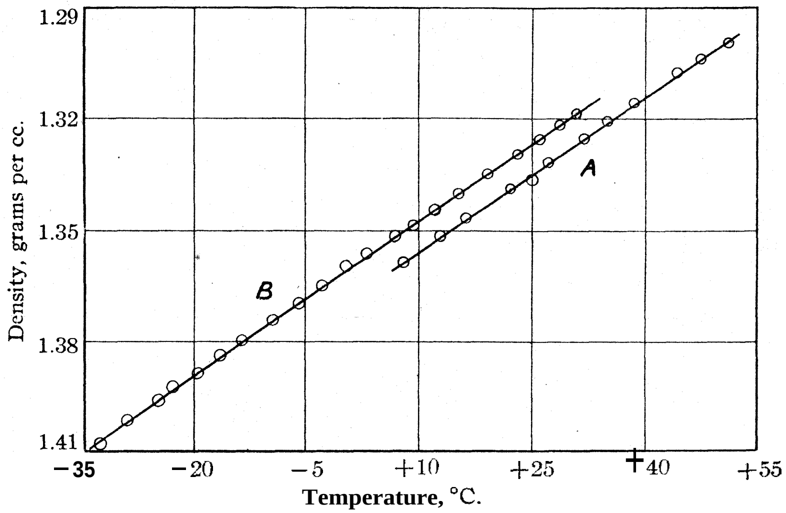

Fig. **4.**

It is obvious that Curve B must be drawn to represent the results of Walton and Whitford, and that Point D does not fall on this curve. This curve represents the solubility of sulfur in hydrogen trisulfide; it has a break at E corresponding to the molecular compound $H_2S_3 \cdot 3S$.

The evidence is strongly in favor of the existence of two chemical compounds H_2S_2 and H_2S_3 and a molecular compound $H_2S_3 \cdot 3S$.

Density.—Two determinations were made of the density and coefficient of expansion of hydrogen disulfide. The first dilatometer had a bulb of 2.73 cc. A scale from a Beckmann thermometer was attached to the stem. Calibration was carried out with water.

The dilatometer was filled with hydrogen disulfide by using a pyrex capillary funnel. The material had been redistilled, but not from phosphorus pentoxide, and was slightly turbid at 0°. The density was determined from S to 51°. The values are tabulated below and are shown in Fig. 4, Curve A.

In the second determination a quartz dilatometer similar to the first was used. The volume of the bulb was 2.08 cc. and of the stem 0.0446 cc. per cm. A reference mark was scratched on the stem about 15 mm. above the top of the bulb. Readings were made by placing the dilatometer so that the stem was in a vertical position and measuring the distance from the reference mark to the bottom of the meniscus with a cathetometer.

Hydrogen disulfide was distilled into the dilatometer from a pyrex still and the apparatus sealed off. A bath of ether stirred by a stream of air was used. Temperatures were measured with a mercury thermometer correct to one-tenth degree. The densities were corrected for the buoyancy of the air. The results are tabulated, and are given in Curve B of Fig. 4. This curve was used for calculating surface tension, since much greater weight must be given to this second determination. A few points lying close to the curves are omitted from the figure.

TABLE V

VARIATION OF DENSITY OF HYDROGEN DISULFIDE WITH TEMPERATURE

Run No. 1		Run No. 2		Run No. 2	
Temp., °C	Density	Temp., °C.	Density	Temp., °C.	Density
7.9	1.3583	−32.5	1.4074	−5.8	1.3697
9.6	1.3557	−31.4	1.4054	−3.9	1.3669
11.0	1.3535	−28.8	1.4012	−2.5	1.3649
12.5	1.3517	−26.9	1.3986	−1.1	1.3635
12.9	1.3515	−24.7	1.3959	0.6	1.3598
14.7	1.3490	−22.6	1.3921	1.7	1.3594
16.3	1.3467	−22.1	1.3918	3.5	1.3563
22.2	1.3386	−21.1	1.3906	5.6	1.3535
25.0	1.3360	−19.3	1.3883	7.2	1.3513
27.3	1.3314	−17.0	1.3853	8.0	1.3503
32.1	1.3250	−16.1	1.3836	9.7	1.3485
35.1	1.3203	−15.5	1.3826	10.8	1.3463
38.7	1.3152	−14.7	1.3816	12.4	1.3442
44.3	1.3072	−13.3	1.3797	14.0	1.3419
45.0	1.3065	−11.8	1.3776	15.4	1.3401
47.4	1.3037	−10.7	1.3761	19.5	1.3347
48.7	1.3015	−9.1	1.3741	23.4	1.3294
51.0	1.2992	−7.8	1.3726	26.3	1.3253
		−6.9	1.3711	29.0	1.3217
				31.2	1.3185

The two values for the density at 15° are 1.341 and 1.348 as compared with Bloch and Hohn's value of 1.376. The purer sample has the lower density and hence it is probable that the disulfide used by Bloch and Hohn contained an excess of sulfur. The density at 0° is 1.3615 and at 25°, 1.3270; the coefficient of expansion is 0.00104.

Vapor Pressures.—For measuring the vapor pressure of hydrogen disulfide a special type of apparatus was needed, since the vapor was decomposed by mercury and the liberated hydrogen sulfide attacked the mercury surface. The apparatus shown in Fig. 5 used a buffer column of air and a soda lime tube in series to protect the mercury surface. A is a 100-cc. flask; B, C and D are bulbs made from pyrex test-tubes. B is provided with a stirrer consisting of a piece of iron wire enclosed in pyrex tubing. C and D are designed so that any liquid distilling from B will collect in the bottom without blocking the connecting tube. E is a pyrex to soft glass ground joint. The manometer was constructed of tubing 1 cm. in diameter. One arm was open to the air. The paper scale was calibrated against a standard steel scale.

Two determinations were carried out with hydrogen disulfide. The disulfide was distilled from A over phosphorus pentoxide into B and a seal made at F. B, C and D were then immersed in a four-liter beaker of water; the stirrer was put in motion and the temperature brought to a suitable point.

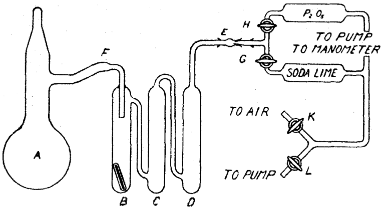

Fig. 5.—Vapor pressure apparatus.

A rough guess was made of the vapor pressure and the manometer set to this point by manipulation of the taps K and L. The apparatus was evacuated by opening H until practically all the air had been driven from C and D by the vapor from the boiling liquid. Tap H was closed and G opened, thus connecting the manometer to the system. Equilibrium was reached within a minute and readings were made of both sides of the manometer and the temperature of the bath. This procedure was repeated until several readings were obtained.

TABLE VI

VARIATION OF VAPOR PRESSURE OF HYDROGEN DISULFIDE WITH TEMPERATURE

First Series

Temperature °C.	Temperature °K.	Pressure, mm. of Hg at 0°	Log P	$1/T \times 10^4$
0.2	273.3	33.3	1.522	36.59
6 8	279.9	44.2	1.645	35.73
10.6	283.7	55.5	1.744	35.25
14.7	287.8	67.1	1.827	34.75
20.1	293.2	87.8	1.944	34.11
24.3	297.4	108.6	2.036	33.62
29.1	302.2	142	2.155	33.09
34.1	307.2	204	2.310	32.55
38 5	311.6	291	2.464	32.09
41 9	315.0	427	2.630	31.75

Second Series

Temperature °C.	Temperature °K.	Pressure, mm. of Hg at 0°	Log P	$1/T \times 10^4$
0.1	273.2	23.9	1.378	36.60
12.6	285.7	54.1	1.733	35.01
24.1	297.2	91.2	1.960	33.65
30.0	303.1	143.6	2.163	32.99
34.0	307.1	187	2.274	32.56
37.2	310.3	202	2.305	32.23
39.8	312.9	277	2.442	31.96
42.5	315.6	273	2.438	31.68
44.6	317.7	315	2.498	31.47

Greater weight was given to the first determination since the stirring was more efficient. Although the observations were carried up to 44°, those above 30° are of little value, due to decomposition of the material in B. When the bath was heated above room temperature, there was considerable difficulty in obtaining correct values, since the liquid distilled into the connecting tubing and decomposed.

The temperature of the bath was taken with a standard mercury thermometer. The readings of the manometer were corrected to 0°. The results are tabulated and shown in Fig. 6. The pressure–temperature curve is merely a smooth curve through the observed points. The log P–$1/T$ curve is a straight line drawn through the observed points. This line passes through the observed value for the boiling point.

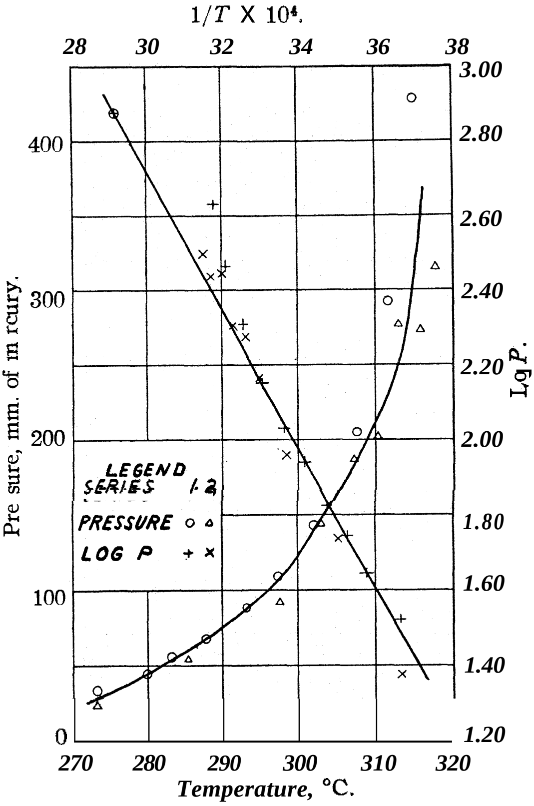

Fig. 6.

The value of the latent heat of evaporation is calculated from the slope of the vapor pressure curve by the formula

$$M\lambda = \frac{2.303 \log (P_1/P_2)}{1/T_1 - 1/T_2}$$

It is found that the molecular heat of evaporation, $M\lambda$, is 8544 cal. and the latent heat per gram, λ, is 129.2 cal.

Boiling Point.—The boiling point of hydrogen disulfide was determined by Bloch and Hohn, and by Walton and Parsons. Since their materials may have been impure and since the vapor came in contact with glass, their values were probably in error by several degrees. It was decided, therefore, to determine the boiling point in an apparatus so designed that the vapor could come in contact only with quartz. The platinum in quartz resistance thermometer (Heraeus type) was placed so that the rubber connection could not come in contact with the vapor.

A sample of hydrogen disulfide was prepared by distillation in a pyrex still from phosphorus pentoxide and transferred into the apparatus. The liquid was heated by a micro flame and boiled quietly for five minutes, the temperature remaining constant. Superheating was prevented by fragments of quartz tubing. Decomposition then started and was detected by a sudden drop in temperature and by a change in the size of bubbles within the liquid.

Owing to a hysteresis effect for the type of thermometer used, the calibration cannot be trusted above room temperature. The platinum thermometer was, therefore, transferred directly from the boiling liquid to a bath of water at approximately the same temperature and compared with a standard mercury thermometer.

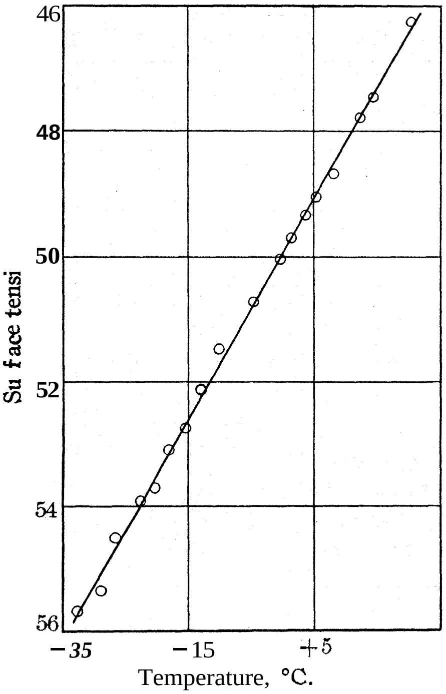

Fig. 7.

The value obtained for the boiling point was 69.9' at 749 mm. A second determination gave 70.6° at 748 mm. The boiling point at 760 mm. may be given as 70.7 ± 0.5°.

From the boiling point and the calculated value for the heat of evaporation the value 24.9 is obtained for Trouton's constant. This value indicates association of the liquid.

Surface Tension.—The surface tension of hydrogen disulfide was determined by measuring the rise in a capillary tube. The liquid was distilled directly into the capillarimeter from a pyrex still and sealed off in *vacuo*. The instrument, built entirely of quartz, is essentially that of Richards.[6] The capillary had an internal diameter of about 1.4 mm. and the wide tube about **13** mm. The constant for the instrument was obtained by a calibration with benzene over a range of temperature.

The capillarimeter was completely immersed in an ether-bath cooled by addition of solid carbon dioxide and stirred by a current of air. The difference in level of the menisci was measured by a cathetometer. Temperatures were measured by a mercury thermometer. The values of the surface tension are tabulated and are given in Fig. 7.

From the smooth curve for the surface tension one may obtain values for

Richards, THIS JOURNAL, 37, 1656 (1915).

TABLE VII

VARIATION OF SURFACE TENSION OF HYDROGEN DISULFIDE WITH TEMPERATURE

Temp., °C.	*Rise*, mm.	*d*	γ	Temp, °C.	*Rise*, mm.	*d*	γ
−32.7	1135	1.406	55.6	− 4 5	10.60	1.367	50.7
−29.0	11 30	1 401	55.3	--0.3	1050	1.361	50.0
−26.8	11.15	1.398	54 5	1 5	10.45	1.359	39.7
−22.8	11.10	1.392	53.9	3.8	10.40	1.355	49.3
−20.5	11.05	1.389	53.7	5.4	10.35	1.354	49.0
−18.2	10.95	1.386	53.1	8.3	10.30	1.350	48.7
−15.9	10.90	1.383	52.7	12.4	10.15	1.344	47.8
−12.9	10.80	1.379	52.1	14.6	10.10	1.341	47.4
−10.1	10.70	1.375	51.5	20.5	9.90	1.333	46.2

calculation of the molecular surface energy, the total surface energy and the Ramsay and Shields constant. The variation of molecular surface energy with temperature is shown in Table VIII.

TABLE VIII

VARIATION OF SURFACE ENERGY OP HYDROGEN DISULFIDE WITH TEMPERATURE

t	γ	*d*	$\gamma(M/d)^{2/3}$
−30	55 10	1 4028	719.1
−20	53.41	1.3890	701.7
−10	51.71	1.3752	683 9
0	50 02	1 3616	666.0
10	48.32	1,3477	647.7
20	46.63	1.3339	630.4

This gives for the Ramsay and Shields constant the value of —1.78. This is lower than the normal value, —2.12, indicating that the liquid is associated. $d\gamma/dt = -0.1695$ and hence the total surface energy, $\gamma + T(d\gamma/dT)$, is 96.3 ergs. The critical temperature may be calculated from the surface tension data; the value found is 278°, which is in good agreement with that calculated from the boiling point. These values cannot be considered as exact, since the liquid is associated.

Heat Capacity.—Measurements were made of the total heats of hydrogen disulfide from various initial temperatures to 25" in an adiabatic calorimeter.

TABLE IX

TOTAL HEATS OF HYDROGEN DISULFIDE BETWEEN 25° AND LOWER TEMPERATURE

Expt.	Initial *temp.*, °C.	*Heat capacity* to +25 00" (cal. *per g*)	Expt.	*Initial* temp., °C.	*Heat* capacity to +25 00° (cal. per g.)
1	0.0	7.62	8	−113.5	63.85
2	− 32.2	18.90	9	−113.5	68.91
3	− 34.2	19.11	10	−115.0	64.80
4	− 78.5	34.09	11	−115.0	69.49
5	− 78.5	34.59	12	−140.0	73.29
6	− 78.5	34.77	13	−184.8	79.71
7	−113.5	63.84	14	−186.8	79.66

A sample of hydrogen disulfide was purified by distillation from phosphorus pentoxide in a quartz still. This sample, contained in a quartz bulb, showed no evidence of decomposition over a period of ten weeks. The apparatus and method of procedure was similar to that of Maass and Barnes.[7] The variation in the temperature of the thermostat in which the disulfide was cooled was less than one degree. The total heat of the quartz bulb from the initial temperature to +25° was obtained from a mean specific heat curve given by Sosman.[8] The results of the determinations are tabulated and are shown in Fig. 8.

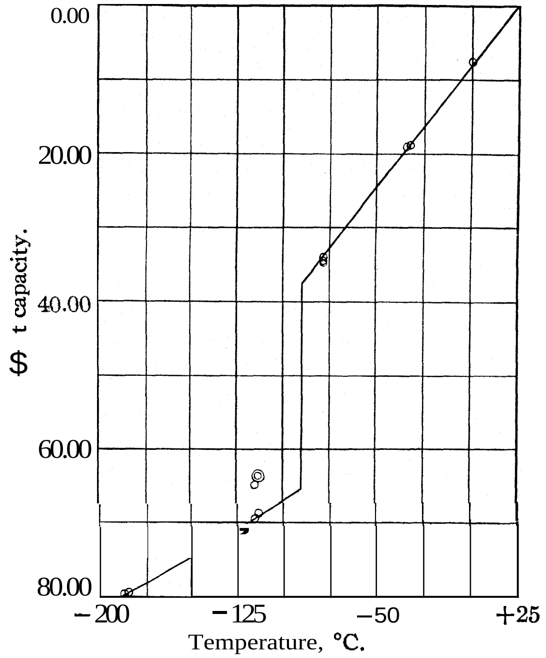

Fig. 8.

The deviation of Expts. 7, 8 and 10 is much too large to be caused by the container not reaching the temperature of the thermostat. It is practically certain that these anomalous results indicate the existence of a metastable crystalline form of hydrogen disulfide. It was impossible to freeze the liquid without supercooling to about −105° and owing to this supercooling the metastable form can exist.

These results permit calculation of the specific heats of the liquid and solid and of the latent heat of fusion.

Specific heat of liquid hydrogen disulfide	0.333
Specific heat of solid hydrogen disulfide	0.142
Latent heat of fusion of hydrogen disulfide	27.3 cal. per g.

Refractive Index.—The refractive index of hydrogen disulfide was measured by an Abbé refractometer. The prisms were carefully washed, using successively benzene, alcohol, hydrochloric acid, water, alcohol and ether. Observations were made over five minutes and the curve extrapolated to zero time. A typical series was

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[7] Maass and Barnes, *Proc. Roy. Soc.* (London), **A111,** *224* (1926).

[8] Sosman, "Properties of Silica," The Chemical Catalog Co., Inc., New York, **1927,** p. 315.

Time, minutes	0:30	1:00	2:00	2:30	3:00	4:00	5:00
Refractive index	1.6326	1.6340	1.639	1.643	1.651	1.659	1.675

The value of the refractive index was found to be $n_D = 1.6322$ at 22°. The molecular refractive power, $R = (n^2 - 1)/(n^2 + 2) \times M/d$ may be calculated and has the value 17.730.

Conclusions

The present investigation allows a number of comparisons to be made between H_2S, H_2S_2, H_2O and H_2O_2.

	H_2S	H_2S_2	H_2O	H_2O_2
Melting point, °C.	-82.9	-89.6	0.0	-0.89
Boiling point, °C.	-59.6	70.7	100.0	151.4
Heat of evaporation	5210	8544	9709	11610
Trouton's constant	24.4	24.9	26.2	27.3
Specific heat of liquid	....	0.333	1.00	0.579
Specific heat of solid	....	0.142	0.45	0.47
Heat of fusion	....	1800	1430	2500
Density at 20°	0.964(-60")	1.3339	0.9982	1.4418
dD/dt	0.00163	0.00138	0.00021	0.00107
Surface tension at b. p.	28.2	38.1	55.9	55.3
Total surface energy	82.2	96.3	113.1	121.0
Ramsay and Shields constant	1.91	1.78	1.08	0.92
Parachor (obs.)	82.9	130.0	52.8	69.6
Parachor (calcd.)	82.4	130.6	54.1	74.1
Refractive index, n_D^{22}	1.384	1.6322	1.3328	1.4139
Molecular refractive power (obs.)	9.64	17.730	3.715	5.900
Molecular refractive power (calcd.)	9.89	17.58	3.725	5.250

The melting point of hydrogen disulfide is a little lower than that of hydrogen sulfide. The melting point of hydrogen peroxide is slightly lower than that of water. The boiling point of hydrogen disulfide is considerably higher than that of hydrogen sulfide; the boiling point of hydrogen peroxide is considerably higher than that of water. The general conclusion is that the change in physical property due to the added sulfur atom in the sulfur compounds is followed in an analogous manner by the change in physical property due to the addition of an oxygen atom in the oxygen compounds. Thus a striking similarity is brought out in the physical properties, as well as the chemical, of hydrogen disulfide and hydrogen peroxide.

Association of the liquids increases in the order H_2S, H_2S_2, H_2O, H_2O_2, the latter two being much more highly associated, as is shown by the Ramsay and Shields constant and the melting point. The agreement of the observed values of the parachor and molecular refractive power with those calculated for the formula H–S–S–H proves that hydrogen disulfide does not contain a double bond or a coordinate bond. The deviation between the observed and calculated values for hydrogen peroxide indicates a possible coordinate bond in this compound.

Acknowledgment is made of a studentship and a fellowship granted to one of us by the Research Council of Canada.

Summary

The preparation and purification of hydrogen disulfide have been described and the conditions investigated for obtaining large yields. It was shown that the higher persulfides are not formed by the solution of sulfur in hydrogen disulfide. The solubility of sulfur in the hydrogen disulfide was measured. The melting point, vapor pressures, density of the liquid, surface tension, refractive index, specific heat and latent heat of fusion of hydrogen disulfide were determined, and related constants were calculated. A comparison of the physical properties of hydrogen sulfide, hydrogen disulfide, water and hydrogen peroxide brings out the relations existing between these compounds.

MONTREAL, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THE NATURE OF THE SORPTION BY CHARCOAL OF GASES AND VAPORS UNDER GREAT PRESSURE

BY JAMES W. McBAIN AND GEORGE T. BRITTON

RECEIVED NOVEMBER 7, 1929 PUBLISHED JUNE 6, 1930

The McBain–Bakr sorption balance[1] has enabled regions of sorption previously inaccessible to be explored with comparative ease. Nearly all studies of sorption have been broken off below atmospheric pressure,[2]

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[1] The microbalance described by McBain and Tanner [*Proc. Roy. Soc.* (London), **A125**, 579 (1929)] has many points of superiority over the McBain–Bakr balance. It is of the beam type, of extreme sensitivity, robust and compact enough to be placed within a glass tube and subjected to great extremes of temperature and pressure while in use.

[2] The chief investigations in which higher pressures have been used are: J. Hunter [*J. Chem Soc.*, 24, 76 (1871)], charcoal with ammonia and cyanogen to 3.5 atmospheres and carbon monoxide to 5.3 atmospheres in a Fontana experiment; E. W. R. Pfeiffer ["Dissertation," Erlangen, 1882, *cf. Beiblatter*, **8**, 630 (1884)], glass wool or charcoal with glass wool in Cailletet's compression apparatus with carbon dioxide or ammonia between 2 and 8 atmospheres, showing no saturation value; Sir James Dewar [*Proc. Roy. Inst.*, *18*, **437** (1906)], 1 g. of charcoal at $-185°$ sorbed 9.3 cc. of hydrogen at 1 atmosphere pressure; this was raised to 13 81, 156.7, 149.3, 145.5 and 138.1 cc. at 5, 10, 15, 20 and 25 atmospheres, respectively; Dewar regarded this as constancy. J. I. Graham [*The Colliery Guardian*, 122, **809** (1921)], carbon dioxide, methane and nitrogen by dry and moist coal up to about 30 atmospheres. The moist sorbed about one-third as much as the dry coal dust, I g. of which, together with a small amount of glass wool, at 30 atmospheres, sorbed about 10 cc. of nitrogen, the amount still apparently rising with increase in pressure. H. Briggs and W. Cooper [*Proc. Roy. Soc.* Edinburgh, 41, **119** (1921)] tested the capacity of steel cylinders partly filled with moist or dry charcoal or silica, using nitrogen, oxygen and hydrogen in some cases up to 100 atmospheres. They found agreement between their results and the Williams–Henry formula, but in some cases the term $k_2 \times x/m$ of that formula was negligible. F. A. Henglein and M. Grzen-

chiefly because of the rapidly growing inaccuracy and uncertainty of measurements where sorption is increasing only slowly with pressure, and the amount of gas or vapor in the poorly defined "dead space" within the apparatus is rapidly becoming the dominant quantity observed.

The present communication describes measurements of the sorption of nitrogen, nitrous oxide and ethylene at pressures up to 60 atmospheres, which were completed at Bristol University, England, early in 1927. The results are of especial interest in that, being carried out with a permanent gas and with vapors above and below critical temperatures and pressures, they enable a decision to be reached between rival views as to the nature of sorption by charcoal.

Experimental

Apart from minor modifications introduced to suit each gas studied, the apparatus consists essentially of the main experimental glass tube A which contains the vapor or gas to be studied and in the upper half of which there is a spiral spring S of fused silica[3] supported from a bent wire C, which is held by friction in the tube, and carrying at its lower end a platinum bucket B filled with charcoal. The temperature of the charcoal is kept constant by means of a thermostat surrounding the upper half of the glass tube. The sorption isotherm is obtained by measuring at a series of pressures the weight of gas sorbed by the charcoal as determined by the increase in length of the silica spring.

Kahlbaum's pure sugar charcoal was used in all experiments after activation either in steam or in air. The former (referred to in another communication[4] as "Wright's Steam D" charcoal) was prepared by heating at 700° in a silica flask for thirty minutes, a current of steam blown against the powdered charcoal, with frequent shaking, at the same temperature for forty-five minutes and the heating continued for ten minutes.

Another portion of the same sugar charcoal was activated by heating in a porcelain tube in an electric furnace at 1140° for twelve hours. During this time a slow stream of air was passed over the charcoal at intervals, so that about 20% of the original charcoal was oxidized. This is elsewhere[5,4] referred to as "Smith's Air C" charcoal.

In all cases the charcoal was evacuated after the apparatus had been set up, keeping the charcoal at 450° by an improvised heating coil[6] of nichrome wire embedded in a hollow tube of asbestos. The vacuum must be applied very slowly to avoid the charcoal blowing out of the bucket. Evacuation was continued until the charcoal had been exposed to a vacuum of less than 10^{-4} mm. for four or five hours. After the charcoal had stood in contact with the nitrous oxide, ethylene or nitrogen at one atmosphere pressure or more for many hours, the evacuation of the charcoal was repeated with the

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kowski [Z. *angew. Chem.*, **38,** 1186 (1925)], ammonia, sulfur dioxide and chlorine by carbon up to several atmospheres.

[3] For details see J. W. McBain and A. M. Bakr, THIS JOURNAL, 48, 690 (1926). Silica fibers about 0.1 mm. thick and one meter long are supplied by the Silica Syndicate

[4] J. W. McBain, H. P. Lucas and P. P. Chapman, communicated to THIS JOURNAL.

[5] J. W. McBain, D. N. Jackman, A. M. Bakr and H. G. Smith, J. Phys. *Chem.*, **34 (1930).**

[6] A strip of asbestos paper about $^1/_{16}$ inch thick soaked in water was wrapped once around a glass tube and the edges kneaded together. Nichrome wire (15 feet, 15 ohms) was wound upon this and covered with further layers of soaked asbestos with the edges well kneaded together. The wet cylinder was slid off the tube by firm pressure and dried by an electric current of about two amperes.

same care as before. This is effective in displacing some of the residual impurities in the charcoal.

Sorption of Nitrous Oxide

The nitrous oxide used was obtained from a small cylinder as supplied for dental purposes.

The sorption tube **A**, Fig. **1**, was **12** mm. in internal diameter, **18** mm. in external diameter and approximately **40** cm. in length and was carefully sealed at the bottom before use, the balance being introduced from the top. Sufficient space was left below the bucket of charcoal so that liquefied gas could be present in excess and yet be far enough from the bucket to allow the temperature of the liquid to be controlled over the range -96.5 to $+20.9°$ without disturbing the temperature of the charcoal. The top of the tube was carefully drawn out, while the tube was in the clamp, until the internal diameter was **1** to 2 mm., the walls being nowhere thinner than **5** mm. on the tapering portion of the tube. The completed sorption tube was sealed onto an apparatus constructed of glass tubing and designed to allow evacuation via tap T_1 and also to allow the admission of nitrous oxide via tap T_2 at pressures up to 80 cm. of mercury. Taps T_1 and T_2 were mercury sealed, and O was a mercury trap which acted as a safety valve.

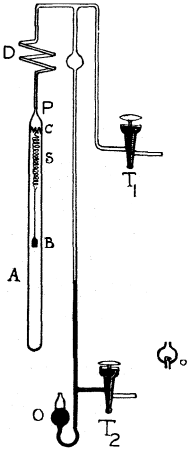

Fig. 1.—The sorption balance connections as used for nitrous oxide.

The general principle of the apparatus described above was due to Mr. H. H. M. Wright, who began the experimental work. His values for the sorption of nitrous oxide at **15°** by steam activated charcoal ("Steam D"), which had been previously evacuated to less than **0.0001** mm. at 470°, were $x/m = 0.099$ and **0.106** at one atmosphere. For the same charcoal evacuated only to **0.007** mm. at **470'** the value of x/m was **0.204** at **19** atmospheres and **15°**.

The silica spring was calibrated both before and after the experiment, but the latter calibration has invariably been used for calculating the results presented. Experience has shown that any considerable elevation in temperature produces a change in the length of such a spring, which decreases in magnitude with time and may be due to the reattainment of an equilibrium of state in the silica disturbed by the heating during bending.[7] The effect is most noticeable in the period of evacuation when the charcoal is heated to **450–500°**. In later experiments on nitrogen and ethylene the spring was not heated during evacuation, the bucket being hung on a fiber **10** cm. long from the end of the spring. It is now our custom to anneal springs for thirty to forty hours at 200° before use, as this is found to remove the effect.

The buckets B were made of the thinnest platinum foil, free from pinholes and supplied by Johnston Matthey and Co., London. They were welded upon a carbon

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[7] I. Sawai and O. Morisawa [*Z. anorg. allgem. Chem.*, *173*, *361* (1928)] found similarly that threads of lead borate glass when first heated to temperatures between **180** and **395°** shrink on account of release of the longitudinal strains produced when they are being drawn. This effect did not occur if the thread were sufficiently loaded. A careful, extensive study of the increase in the elastic constants of fused quartz upon heating has recently been published by H. D. H. Drane, *Proc. Roy. Soc.* (London), **122A,** 274 (1929). See also the data of the Bureau of Standards quoted in *Ind. Eng. Chem., News Edition,* **8,** 14 (1930).

rod as a form and were about 15 mm. deep and 5 or 6 mm. in diameter, weighing from 0.09 to 0.12 g. and holding about 0.12 g. of charcoal.

A Kaye–Backhurst steel mercury pump, backed by a Cenco "hyvac" pump, was used, the combination readily producing 10^{-5} mm. The pumps were joined to a wide tube branching into mercury sealed taps, one of which was T_1, Fig. 1; another led to a McLeod gage reading to 10^{-5} mm. and a Pirani gage, while a third tap led to a tube of calcium chloride and phosphorus pentoxide by which air could be admitted when desired without admitting moisture.

After the second evacuation, the charcoal and tube were allowed to cool, while tap T_1 was left open, the length of the spring S read carefully with a Wilson traveling microscope,[8] three or four concordant values being obtained, and from this value the weight of gas free charcoal was calculated.

In order to introduce the nitrous oxide into the apparatus, the lower tip of the sorption tube A, Fig. 1, was cooled in liquid air, and the gas was supplied at about 80 cm. of mercury pressure through tap T_2. The mercury trap O acted as a safety valve, preventing a rise of pressure when the level of the liquid air fell, or the rate of condensation decreased for any other reason. The liquid air level was gradually raised until a column of solid nitrous oxide about 4 inches deep was obtained. Tap T_2 was then closed and T_1 opened. Tube A was pumped out to about 2 mm. and refilled with nitrous oxide several times to remove traces of nitrogen likely to come from the nitrous oxide cylinder. The sorption tube was then sealed off at P under vacuum and set up in the screen, Fig. 2. After sealing off the capillary tube, it was found advisable not to allow the internal pressure to rise above atmospheric for twelve hours. In nearly every case impatience led to blowing off the tip at some stage of the experiment.

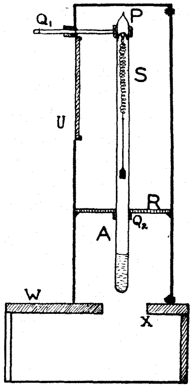

Fig. 2.—Protecting screen.

The screen, Fig. 2, consisted of a sheet-iron box 6 inches square and 18 inches long, having one side removable by undoing nuts and opening only at one end. A slit U, 0.5 inch wide, was cut in the face opposite the removable one, and a sheet of plate glass 0.25 inch thick fitted behind the slit. The box stood on the open end with slit to the front. Above the slit and also in one side about 6 inches from the bottom, two brass cylinders of 1-inch diameter were mounted. They were drilled so that the brass rods Q_1 and Q_2, 0.25 inch in diameter, could slide in them. Two ends of a steel helix were secured to the end of each rod like a spring fountain pen clip so that the tube could be slid into them and be firmly held without straining the glass. Since these rods were at right angles, it was possible to adjust the tube A very easily and allow the spring S to swing freely. An asbestos partition R was mounted below the level of the bucket and nichrome coils were introduced above the partition so that the bucket and charcoal could be warmed to any desired temperature. The screen stood upon a bench W about 7 inches high, 15 inches wide and 18 inches long, having a hole X cut in the top. In operation a Dewar vessel was raised through X to surround the liquid nitrous oxide, and the door of W replaced.

A Dewar vessel containing carbon dioxide snow and ether was used as a bath for maintaining the liquid nitrous oxide at any desired temperature below 0°. Stirring and frequent small additions of solid carbon dioxide sufficed to keep the temperature constant within 0.5" of the desired value. The temperatures were observed by a pentane thermometer which was calibrated at the time of performing the experiment by ob-

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[8] W. Wilson, Gourley Works, Seven Sisters Road, South Tottenham, London, E. C., England. This microscope could be read to ±0.001 cm.

serving the freezing points of pure liquids. The vapor tension corresponding to the observed temperature of the liquefied nitrous oxide was obtained from the vapor tension–temperature graph determined in a previous paper,[9] and the length of the spring S was read by the traveling microscope after an interval of not less than two hours since the last change in temperature of the bath. It was found that no change in length of the spring occurred over longer periods, and values of sorption approached from either side of the equilibrium lay on the same curve. Since the same traveling microscope was used for calibrating the springs as for taking sorption measurements, no calibration of the scale was necessary, as any errors were automatically eliminated. Care was taken that all final movements of screws for fine adjustment of height or focus were carried out in the same direction. For higher pressures, necessitating baths with temperatures above 0°, mixtures of tap water and ice water were used and were maintained constant by occasional addition of small quantities of ice water.

The data for nitrous oxide are tabulated in Tables I–III, in which T is the temperature of the liquid nitrous oxide in degrees centigrade, and p is the corresponding vapor tension in atmospheres. To save space, only the first part of Table I is given in full. The apparent weight of gas sorbed, given as x uncorrected in Table I, equaled the difference in length of the spring at pressure p and the zero reading $(L_p - L_o)$ divided by the sensitivity of the spring. The sensitivity of the spring is ten times the extension produced by 0.1 g. increase in load. A correction for buoyancy must be made.

TABLE I

SORPTION OF NITROUS OXIDE BY "STEAM D" CHARCOAL. TUBE III

Mass of charcoal, m = 0 1023 g. Sensitivity of spring, S = 15.25 cm /g. Total volume of charcoal and platinum bucket, 0.06087 cc.

T, °C.	p, atm.	ρ G/cc.	$L_p - $ Lo, cm.	x (uncorr), g.	Buoyancy, g.	x (corr), g.	x/m
Temperature of charcoal, 20°. Zero reading of spring, S = 8.647 cm.							
−96.5"	0 6	0 000923	0 237	0 01554	0 00006	0 0156	0 153
−87 0	1 1	00204	233	01528	,00012	.0154	.151
−72.5^a	2.4	,00449	274	.01797	,00027	0182	.178
−62 0	4 0	00758	.288	.01889	00046	.0194	.189
− 505"	6 3	0123	282	.01849	.00075	0192	.188
−41 5	8 8	0178	.280	.01836	.00109	.0195	.190
−39.0"	9 7	.0199	.289	01895	,00121	.0202	.197
−30.5	130	.0280	287	01882	,00170	.0205	.201
−18 0"	19 3	.0450	278	,01823	.00274	.0210	.205
−18.0"	19 3	.0450	.278	.01823	.00274	.0210	.205
−18 0^a	19 3	.0450	.285	,01869	00274	.0214	.210
−17 0^a	19 8	.0464	.279	.01830	.00283	.0211	.207
+ 0 5"	31 1	.0814	.255	.01672	,00496	.0217	.212
+ 0 5	31 1	0814	.251	.01646	00496	.0214	.209
+ 3 8	33 4	0895	.246	01613	00545	0216	.211
+ 7 4	36 3	.100	233	01528	.00611	.0214	.209
+ 9 4	380	.107	225	01475	00650	.0213	.208
4-12 9	41 6	.122	215	01410	.00741	.0215	.210
+13.9	428	127	.205	.01344	,00772	.0212	.207

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[9] G. T. Britton, Trans. *Faraday Soc.*, 25, 520 (1929).

TABLE I (*Concluded*)

T, °C.	*p*, atm	Buoyancy, g.	*x/m*	T, °C	*p*, atm	Buoyancy, g.	*x/m*
Temperature of charcoal, 45°							
−84 0"	1 3	0 00013	0 126	+ 0 2[a]	30 8	0.00388	0.186
− 840	1 3	.00013	.115	+13.2	420	.00582	.192
−42.5"	8 5	.00090	167	+14 3"	43 5	.00608	.189
−40.5"	9 1	,00096	.170	+14.5	438	.00614	.193
−22 5[a]	16 9	00187	17.5	+17 5	48 6	.00692	.191
+ 0 2	30 *8*	00388	186	+19 5	49 7	.00707	.185
Temperature of charcoal, 67°							
−88.0"	1 1	0000106	0.0869	4-02"	30.8	0 00360	0 174
−49.5	6 6	00065	.151	+12 9	41 6	.00506	1ia
−45.3"	7.7	.00076	141	4-20 9	51 3	00618	172
−37.0"	103	.00103	.154				

[a] Desorption experiment.

TABLE II

SORPTION OF NITROUS OXIDE BY "STEAM D" CHARCOAL. TUBE IV

Mass of charcoal, $m = 0.1463$ g. Sensitivity of spring, $S = 22\ 50$ cm./g. Total volume of charcoal and platinum bucket, 0.08618 cc.

T,°C.	*p*, atm.	Buoyancy, g.	*x/m*	*T*,°C.	*p*, *atm*	Buoyancy, g	*x/m*
Temperature of charcoal, 20°							
−88.0[a]	1.1	0.00018	0.148	−23.0	16.6	0.00323	0.200
−78.5[a]	1.8	.00029	.150	−13.0	21.9	.00452	.200
−77.0[a]	2.0	.00032	.160	+ 0.2[a]	30.8	.00693	.210
−69.5	2.8	.00045	.181	+ 0.2[a]	30.8	.00693	.210
−65.0	3.5	.00057	.183	+ 1.8	32.0	.00728	.205
−53.0	5.8	.00097	.191	+ 8.4	37.1	.00890	.202
−47.0[a]	7.3	.00125	.189	+12.9[a]	41.6	.01049	.206
−41.5[a]	8.8	.00154	.193	+13.9[a]	42.8	.01093	.203
−33.0	11.9	.00218	.199	+14.6	43.8	.01131	.207

[a] Desorption experiment.

TABLE III

SORPTION OF NITROUS OXIDE BY "STEAM D" CHARCOAL TUBE V

Mass of charcoal, m = 0 0943. Sensitivity of spring, $S = 12\ 02$ cm /g Total volume of charcoal and platinum bucket, 0.05644 cc

T, °C.	*p*, atm.	Buoyancy, g	*x m*	*T*,° C	*p*, atm	Buoyancy, g	*x/m*
Temperature of charcoal, 20°							
−77 0"	2 0	0 00021	0 162	−18 0[a]	19 3	0 00254	0.214
−75.5"	2 1	00022	161	+ 0 1[a]	30 7	00452	.218
−74 0	2 3	.00024	171	+ 1.6	319	00475	.218
− 64.5	3 5	.00037	195	+ 9 6[a]	*38 1*	00605	.208
−55.5[a]	5 2	00056	198	+10.9	394	00636	.211
− 55.5	5 2	00056	191	+15 5	45 1	.00773	.208
−43.5	8 2	00093	202	+17.7	490	00870	.214
− 290"	13.7	.00168	.209				

TABLE 111 *(Concluded)*

T, °C.	p, atm.	Buoyancy, g.	x/m	T, °C.	p, atm.	Buoyancy, g.	x/m
Temperature of charcoal, 45°							
−74.5"	2.2	0.00021	0.127	−17.5	19.5	0.00204	0.187
−57.5"	4.8	.00046	.163	−16.6	20.0	.00210	.184
−53.0	5.8	.00056	.150	+ 0.2[a]	30.8	.00360	.193
−45.0"	7.8	.00076	.169	+ 8.4	37.1	.00459	.192
−40.5"	9.1	.00089	.167	+16.6	46.7	.00614	,185
−27.0	14.6	,00147	.179	+17.0	47.7	.00629	.187
Temperature of charcoal, 67°							
−77.0"	2.0	0.000179	0.0910	+ 0.8	31.3	0.00340	0.179
−71.5	2.5	.00022	.110	+11.6	40.1	.00452	.179
−57.0	4.9	.00044	.129	+16.6	46.7	.00526	.177
+ 0.2[a]	30.8	.00334	.170	+17.1[a]	47.8	.00538	.174
+ 0.8[a]	31.3	,00340	.179	+18.3	48.5	.00545	.175

[a] Desorption experiment.

Data for the density of the vapor of nitrous oxide are given in a previous communication.[9] From the plot of pv against p the values of density in g./cc. appropriate to the pressures used in obtaining points on the sorption isotherm were calculated. These are given as ρ in Table I. The total volume displaced in cubic centimeters (the volume of the platinum composing the bucket plus the volume of the charcoal it contained) multiplied by the density gave the buoyancy correction in grams. This was added to the apparent sorption *(x* uncorrected), and the sum (x corrected) was divided by the mass of charcoal m to give values of sorption designated as x/m in the tables. The volume of the charcoal was calculated from its mass in vacuo by assuming 1.8 g./cc. as its density.

Sorption of Ethylene

The apparatus for measuring the sorption of ethylene was essentially the same as that used for nitrous oxide. Ethylene condenses very much more slowly than nitrous oxide, and hence it was condensed at 2 to 3 atmospheres pressure. Between the sorption tube A and the glass spiral D, Fig. 1, a glass T-piece of capillary tubing was introduced. The third leg of this was bent downward and again branched (see Fig. 3). At the ends of the branches two swellings were made in order that pressure tubing could be wired on safely. The swellings were drawn down into thin tips G and G_1 which were sealed and a slight scratch made on them with a file. Tip G was connected by pressure tubing Y to a closed-end mercury manometer and a cylinder of ethylene, the connecting tubing having first been swept free of air by a current of ethylene.

After the preliminary evacuation ethylene was admitted by turning open the valve of the gas cylinder and breaking the tip G. As G was so fine, no sudden rush of gas took place. The rubber connection was then transferred to the other leg and the fine tip G sealed by a small flame.

Following the second evacuation, the sorption tube was drawn off at Z, and ethylene was introduced via G_1 as before. A Dewar flask of liquid air was placed so that the lower end of the sorption tube just dipped in it, and the ethylene pressure raised to 2 or 3 atmospheres. From time to time the Dewar vessel was raised a little until a suitable depth of ethylene was obtained. Impurities in the gas were swept out by allowing the solid ethylene to melt and boil off, G having been opened. The sorption tube was then sealed off under a slight vacuum obtained by slipping over G a rubber connection to the pumps.

In order to obtain the sorption isotherm of ethylene at 0°, a piece of glass tubing, 2.5 inches in diameter, was drawn down to a neck which would just slide over the sorption tube. A length of 5 inches was left on the neck, and the resulting jacket, which gave a water-tight joint, was secured by a short piece of rubber tubing to the sorption tube at the point where the bucket of charcoal was suspended. This jacket was kept packed with ice. The spring S was thus at room temperature, the charcoal at 0°, and the end of the sorption tube containing the liquid ethylene could still be kept at any desired temperature with carbon dioxide and ether mixtures.

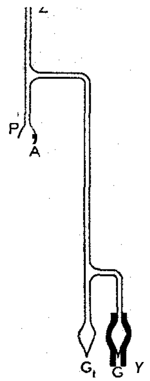

Fig. 3.—Capillary tubing introduced in apparatus for sorption of ethylene.

TABLE IV

SORPTION OF ETHYLENE BY "AIR C" CHARCOAL. TUBE II

Mass of charcoal, m = 0.0789 **g. Sensitivity of spring,** S = 14.06 cm./g. **Total volume of charcoal and platinum bucket,** 0.04825 **cc.**

T, °C.	p, atm.	Buoyancy, g.	x/m	T. °C.	p, atm.	Buoyancy, g.	x/m
Temperature of charcoal, 0°							
−73.0	4.8	0.00031	0.188	−12.5	29.5	0.00274	0.224
−55.7	9.3	.00063	.209	−10.7	30.8	.00293	.222
−30.5	19.5	00154	.225	− 5.5	34.9	.00358	.222
−28.5	20.5	.00164	.226				
Temperature of charcoal, 20°							
−77.0	4.1	0.00024	0.176	−32.5	18.6	0.00127	0.214
−73.0	4.8	.00028	.186	−25.0	22.2	.00158	.210
−61.0	7.6	.00046	.186	−16.0	27.3	.00207	.214
−57.5	8.7	.00054	.194	− 9.5	31.7	.00254	.208
−49.5	11.5	.00073	.202	0	39.9	.00358	.209
−37.5	16.3	.00109	.203				
Temperature of charcoal, 45°							
−79.0	3.8	0.00020	0.161	−24.5	22.5	0.00143	0.198
−61.0	7.6	.00042	.175	−10.5	30.9	.00213	.200
−49.5	11.5	.00066	.182	− 8.0	32.9	.00232	.201
−42.5	14.2	.00084	.186	0	39.9	.00298	.201
−34.5	17.7	.00108	.198				

TABLE V

SORPTION OF ETHYLENE BY "AIR C" CHARCOAL. TUBE III

Mass of charcoal, m = 0.1051 g. Sensitivity of spring, S = 19.94 cm./g. Total volume of charcoal and platinum bucket, 0.06288 cc.

T, °C.	p, atm.	Buoyancy, g	x/m	T, °C.	p, atm	Buoyancy. g	x/m
Temperature of charcoal, 0°							
−78.0	4 0	000033	0.163	−31 7	19 0	0 00194	0 206
−54.5	9 7	.00087	.189	− 250	222	00237	209
−44.5	13 4	.00126	.198	− 163	271	00314	206
−42.5	14 2	.00135	.201	− 120	299	00364	202
Temperature of charcoal, 20"							
−88 0	2 5	0.00019	0.148	−29.7	19 9	0 00180	0 182
− 637	6 9	.00054	.166	−22.5	23 5	00222	193
−52.0	107	.00088	.170	−10 7	30 8	,00318	.191
−49.4	116	.00096	.174	0	39 9	.00466	.191
−37 0	16 5	,00144	.185	+ 3.0	429	00524	191
Temperature of charcoal, 45°							
−82.0	3 3	000023	0.132	−11.7	30.2	0.00270	0 169
− 480	121	.00091	.148	− 9 5	31 7	,00287	166
− 280	208	.00170	.158	0	39 9	00389	169

The experimental data found for ethylene are given in Tables IV and V. Tube I burst, which prevented the calibration of the spring from being checked. All calculations were made exactly as for nitrous oxide, and the pressure p and the density were obtained from vapor tension–temperature and p–pv graphs, respectively, which had been determined in the previous communication already mentioned in the case of nitrous oxide.

Sorption of Nitrogen

Mr. H. H. M. Wright placed the balance in a steam boiler water-level gage secured to a heavy iron stand. A passage in the upper casting communicated from the packing gland to a copper tube leading from a cylinder of compressed nitrogen via a constant pressure gas regulator. Another passage led to a gas valve by which the apparatus could be connected to the vacuum pumps by pressure tubing or isolated from them as desired. A passage in the lower casting led to a large brass cylinder bolted by a flanged joint to the casting. The silica spring was placed in the glass tube and the platinum bucket containing charcoal was suspended inside the brass cylinder by a fine fiber from the spring. A small electric heater, made by winding nichrome wire on a silica glass tube, fitted inside the cylinder and heated the charcoal to the desired temperature. This heater was calibrated before use. The leads for the heating current were led through the gaskets between the flanges, which were water-cooled to prevent decomposition of the rubber in the packing gland. Wright's data for nitrogen are graphed in Fig. 4.

A better type of apparatus was then devised. It was necessary to seek a better method of uniting glass and metal with a vacuum and pressure tight joint. Many possible joints[10,11] are described in the literature, but none were successful. A much simpler joint, Fig. 5, which is highly efficient and very easily made, was developed. A cylinder of brass 7 cm. long was drilled out to slide over the given capillary tube N (approximately 7 mm. in diameter), and a length of about 5 cm. was drilled out to 1.5 cm. diameter and tapped to take a small packing nut I, which just slipped over the capillary tube. The copper tube F was soldered into H, and the whole inverted. The capillary N was placed in position, and the brass warmed to the softening point of a good sealing wax. Sealing wax was then melted in until the space was filled, and the hot nut I screwed in about four turns, squeezing soft wax between the brass and the glass, where they were a close fit. The joint was allowed to cool without disturbance and was then ready for use. Such joints have held vacuum to 0.0005 mm. and internal pressures up to 65 atmospheres without any sign of failure or flowing of the wax. They will stand much vibration and rough treatment without failure. Waterston's "Bee Brand" Prize Medal sealing wax proved highly satisfactory.

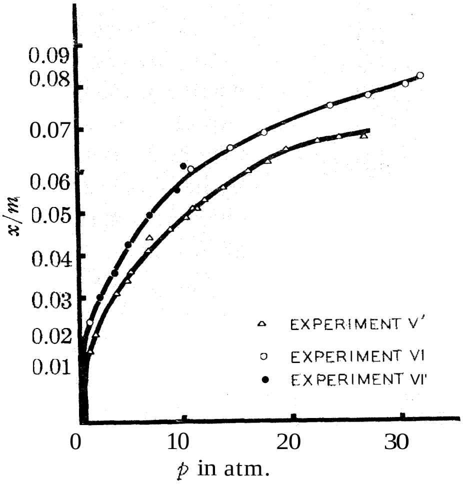

Fig. 4.—Wright's data for sorption of nitrogen by "Steam D" charcoal at 15°. Temperature of evacuation of charcoal is 500°. In Experiment V′, vacuum obtained is 0.6 mm. and time of evacuation is nineteen hours In Experiments VI and VI′, vacuum attained is 0.02 mm and time of evacuation is twenty-four hours

The sorption tube used in these experiments for measuring the sorption of nitrogen was of the same dimensions as that used for nitrous oxide but was carefully drawn out to a thick capillary at the lower end L, Fig. 6. After the introduction of the balance through the top, the upper end of the sorption tube was drawn to a thick capillary and fused onto a glass capillary N which was joined to a copper tube F by means of the special joint J (compare Fig. 5).

A small gas cylinder D, Fig. 7, was surmounted by a brass manifold carrying two good gas regulating valves V_1,V_2 and a pressure gage K reading

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[10] M. L. Dundon, THIS JOURNAL, 45,716 (1923).

[11] E. C. McKelvy and C. S. Taylor, *ibid.*, 42, 1364 (1920).

to 150 atmospheres. V_2 was connected to a large gas cylinder E, and V_1 was joined to the copper tube F. The valves were carefully packed with leather washers and vacuum grease and proved capable of holding a vacuum of 0.0005 mm. The cylinders, valves, gages, unions and copper leads were supplied by the British Oxygen Company and proved satisfactory in use. The nitrogen, which had a purity of 99.5%, was obtained from the same company in cylinders charged to 120 atmospheres. This method of gas control was adopted because the automatic gas regulator previously used by Mr. Wright was very troublesome, allowing the pressure to rise slowly. Leaks, which were rare and slight, were readily compensated by hand operation before the pressure had changed more than a fraction of one atmosphere.

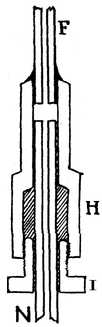

Fig. 5.—A vacuum- and pressure-tight joint for uniting glass and metal by means of sealing wax.

The glass portion of the apparatus was enclosed entirely in a sheet-iron screen with a slit covered by plate glass. A sheet of iron $^1/_{16}$ inch thick was bent into a box of square section 4" X 4" with the opening at the back. The opening was sprung out wider to pass the tube and clamp when placing the screen in position and was closed by means of wire tied around the screen.

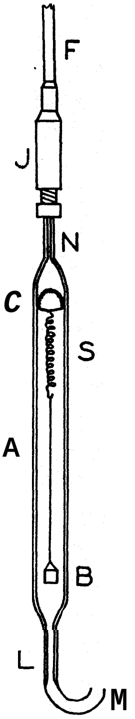

Fig. 6.—The sorption balance as used for nitrogen.

For the evacuation or outgassing of the charcoal the capillary tube L, Fig. 6, was fused to a tube M leading to the vacuum pumps. The charcoal was heated to 450° by an electric heater, and the pumps started up as described for the experiments with nitrous oxide. The valve V_1, Fig. 7, was shut during this operation. The time of evacuation was considerably longer than for nitrous oxide as, owing to small leaks, the pumps were much longer in reaching a low enough vacuum. In view of the number of mechanical joints, any pressure below 10^{-3} mm. was regarded as satisfactory, and outgassing was carried out for four to five hours at the lowest pressure obtainable. After the first outgassing, nitrogen was passed in via V_2 and V_1 from E until the pressure was one atmosphere. After fifteen hours the evacuation was repeated, the charcoal cooled, and the zero reading taken as for nitrous oxide. The tube L, Fig. 6, was carefully warmed up by the blowpipe and sealed off under vacuum, the pumps still running to carry off any gases or vapor given off by the glass.

While measuring the sorption of nitrogen, the valve V_1, Fig. 7, was always left open. The main valve of E was opened, and gas admitted by V_2

into D and A up to any desired pressure as read on K. The cylinder D served to prevent violent inrushes of gas, as its size demanded a considerable quantity of gas to produce small pressure changes. Moreover, any small leakage at valves or unions would be minimized and readily made up by small additions of gas by V_2. The length of the spring S was read after an interval of not less than one hour. A shorter period can be permitted in this experiment than in the nitrous oxide experiment, because there is no liquid–vapor equilibrium to establish in addition to the gas or vapor–solid equilibrium, the pressure being put at its final value in a minute or so. When equilibrium had been approached from both sides, the pressure was lowered by undoing a union or the packing gland of V_2 and allowing gas to leak out. This was more satisfactory than introducing another valve.

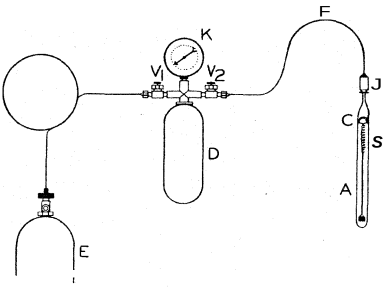

Fig 7.—Method of gas pressure control used in sorption of nitrogen

The results were calculated exactly as for nitrous oxide. The density of the nitrogen at 20° was calculated from the data on the compressibility of the gas as measured by Amagat[12] at 16°, taking 1.1650 as the density at 20° and one atmosphere pressure. By plotting the density–pressure graph up to 60 atmospheres, the density of the nitrogen at any pressure could be readily obtained.

The densities for nitrogen at −77° were calculated from the compressibility data of van Urk.[13] The equation of state of nitrogen is given as

$$PV_A = A_A + \frac{B_A}{V_A} + \frac{C_A}{V_A^2} + \frac{D_A}{V_A^4} + \dots$$

in which $A_A = 1.00043\ (1 + 0.0036618\,t)$, t being the temperature in degrees centigrade. P is in international atmospheres and V is in normal volume units at 0°. A table of values of B, C, D, etc., is given for various temperatures. The values of the constants B, C, D appropriate to the temperature of −77° were obtained by graphical interpolation. The final equation is thus

$$p = \frac{0.7206}{V} - \frac{1.115 \times 10^{-3}}{V^2} + \frac{2.682 \times 10^{-6}}{V^3}$$

the fourth term having proved negligible. By commencing with unit volume at 0°, 1 atmosphere pressure and density ρ_0 and by substituting fractions x such as 0.25, 0.025, 0.015, 0.01, etc., for V, the corresponding value of P is obtained. Obviously the density ρ of the gas at −77° under

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[12] E. H. Amagat, "International Critical Tables," Vol. III, 1928, p. 17.

[13] Th. van Urk, Communications from the Physical Laboratory of the University of Leiden, No. 169e, p. 50 (1924).

the pressure P is ρ_0/x, x being the fraction of the volume corresponding to P. The density of nitrogen under standard conditions has the value of 1.25057 grams per liter.

The experimental data obtained from the measurements of the sorption of nitrogen by charcoal are tabulated in Tables VII–X, while Table VI contains a comparison of the conditions of outgassing the charcoal.

TABLE VI

CONDITIONS OF OUTGASSING THE CHARCOAL BEFORE MEASURING THE SORPTION OF NITROGEN

Expt.	Charcoal	Time for const. vacuum, hours	Press., mm.	Time at press., hours	Final press., mm.	Temp. of evacn., °C.	Contact cold N_2, hours
			First Evacuation				
I	Steam D	4	0.0025	2	0.0025	450	16
II	Steam D	8	.0003	12	.0025	490	16
III	Air C	18	.0002	6	.0002	490	16
IV	Air C	3	.0002	8	.0002	490	60
			Second Evacuation				
I	Steam D	3	0.001	4	0.001	450	..
II	Steam D	8	.0005	4	.0005	490	..
III	Air C	4	.0003	6	.0002	490	..
IV	Air C	3	.0001	4	.0001	490	..

In the case of Bxperiment IV the charcoal was outgassed for ten hours at 460° and 0.001 mm. vacuum, which could not be improved upon owing to a crack in a glass seal. To put this right, air was admitted, and the charcoal was cooled and re-evacuated as above ten hours later.

TABLE VII

SORPTION OF NITROGEN BY "STEAM D" CHARCOAL. TUBE I

Mass of charcoal, $m = 0.0960$ g. Sensitivity of spring, $S = 22.55$ cm./g. Total volume of charcoal and platinum bucket, 0.05859 cc.

p, attn	*x* (uncorr.), g.	*x* (corr.), g.	*x/m*	*p*, atm.	*x* (uncorr.), g.	*x* (corr.), g.	x/m
			Temperature of charcoal, 20°				
1 0^a	0.002084	0.00215	0.0224	23.0"	0.005188	0.00676	0.0705
1.5	.002749	.00285	.0297	25.0	.005055	.00677	.0705
2.0^a	.003237	.00337	.0351	30.0"	.005011	.00707	.0737
5.0	.004169	.00451	.0470	32.0	.005055	.00725	.0755
5.0"	.003991	.00433	.0451	37.0^a	.004967	.00751	.0782
7.0	.003991	.00447	.0466	38.0	.004967	.00758	.0790
9.0^a	.004213	.00483	,0503	42.7"	.004745	.00769	.0801
10.0"	.004834	.00552	.0575	46.0	.004435	.00761	.0793
11 0	.004789	.00555	.0578	49.0"	.004435	.00782	.0814
12.5"	.004967	.00582	.0607	52.0	.004257	.00785	.0818
13.5	.005144	.00607	.0632	56.0"	.003947	.00781	.0813
16.5"	.005188	.00632	.0658	61.0	.003636	,00784	.0816
20.0	.005100	.00647	.0674				

[a] Desorption experiment.

TABLE VIII

SORPTION OF NITROGEN BY "STEAM D" CHARCOAL. TUBE II

Mass of charcoal, m = 0.0905g. Sensitivity of spring, S = 19.76 cm./g. Total volume of charcoal and platinum bucket, 0.05556 cc.

p, atm.	x (uncorr.), g.	x (corr.), g.	x/m	p, atm.	x (uncorr.), g	x (corr.), g.	x/m
Temperature of charcoal, 20°							
1 0	0.001063	0 00113	0.0125	16.0	0.004504	0.00554	0.0613
1.1[a]	.001670	.00174	.0193	17.0	.004656	.00576	.0637
3.0	.002075	.00227	.0251	22.5"	.005061	.00652	.0721
5 0[a]	.002429	.00275	.0304	26.5	.005010	.00673	.0744
6.0	,003492	.00388	.0429	31.5	.004960	.00701	.0775
6.5	.003036	,00346	.0382	35.2"	.005263	.00756	.0835
9.0"	.003694	.00428	.0473	37 0	.005314	.00773	.0854
11.0	.004049	.00477	.0527	43 5	,005213	.00806	.0890
13.5"	.004302	.00518	.0572	53.0	.004656	,00812	.0898

[a] **Desorption experiment.**

TABLE IX

SORPTION OF NITROGEN BY "AIR C" CHARCOAL. TUBE III

Mass of charcoal, m = 0.0946g. Sensitivity of spring S = 15.08 cm./g. Total volume of charcoal and platinum bucket, 0.06248 cc.

p, atm.	x (uncorr.), g.	x (corr.), g.	x/m	p, atm.	x (uncorr.), g.	x (corr.), g.	x/m
Temperature of charcoal, 20°							
1.0	0.002255	0.00233	0.0246	20 8	0.007228	0.00875	0.0925
4.1"	.003448	.00375	.0396	31 0	.007692	,00996	.105
6.0	.004509	.00495	.0523	33 2[a]	.007958	.0104	.110
10.8	.005504	.00629	.0665	40 9	.007825	.0108	.115
11.0	.005968	.00677	.0716	46.7	.007958	.0114	.120
18.5[a]	.007095	.00845	.0893	50.6	.007692	.0114	.121
20.6"	.007493	.00900	.0951				
Temperature of charcoal, -77°							
3.5	0.01154	0.0119	0.126	33.5"	0.01558	0.0195	0.206
10.0	.01499	.0161	.170	39.2	.01499	.0196	.207
16.7	.01625	.0181	.192	48.0	.01412	.0199	.211
25.7[a]	.01625	.0192	.203				

[a] **Desorption experiment.**

TABLE X

SORPTION OF NITROGEN BY "AIR C" CHARCOAL. TUBE IV

Mass of charcoal, m = 0.0851g. Sensitivity of spring, S = 19.40 cm /g. Total volume of charcoal and platinum bucket = 0.05178 cc.

p, atm.	x (uncorr.), g.	x (corr.), g.	x/m	9, atm.	x (uncorr.), g.	x (corr.), g.	x/m
Temperature of charcoal, 20°							
1.0	0.004897	0.00496	0.0583	19.1	0.008608	0 00976	0 115
1.0'	.004433	.00450	.0528	31.0	.008866	.0108	.126
6 0"	.005979	.00634	.0745	40.0[a]	.009072	.0115	.135
11 1	.007629	.00830	.0976	50.2"	.008866	0119	.140
15 5	.007526	.00846	.0995	58.5	.008918	.0125	.147

TABLE X (Concluded)

p, atm.	x (uncorr.), g.	x (corr.), g.	x/m	p, atm.	x (uncorr.), g.	x)corr.), g	x/m
Temperature of charcoal, −77°							
1.0	0.009124	0.00921	0.108	25.0	0.01758	0.0195	0.229
8.0[a]	.01479	.0155	.182	29.3"	.01861	.0214	.252
10.0	.01546	.0164	.192	*35.0"*	.01840	.0218	.256
13.3[a]	.01716	.0184	.216	35.0	.01814	.0215	.253
17.0	.01778	.0194	.228	44.0	.01747	.0218	.256
17.0[a]	.01716	.0187	.220	48.1"	.01711	.0219	.257
20.6	.01814	.0200	.236	54.5	.01644	.0219	.257

[a] Desorption experiment.

Discussion

The data portray true reversible equilibria, because points on the curves obtained by sorption or by desorption are indistinguishable within the experimental error. The experiments were always sufficiently prolonged for this to be the case. Somewhat higher values, less affected by high pressures, would probably have been obtained had we taken even greater precautions in the preliminary evacuation of the charcoal.[14]

The first half of the total sorbed material is taken up at low pressures, almost infinitesimal in the cases of nitrous oxide and ethylene, but we are concerned here with the behavior in the higher regions of pressure. Here the buoyancy correction for the density of the gas or vapor becomes important. This was very clearly shown in the unabridged tables where neglect of the buoyancy correction causes the uncorrected values of the sorption x to pass through a maximum and then fall off with further increase of pressure. To evaluate the correction it is necessary to know the density of the charcoal. Unfortunately, this is a matter of extreme divergence of opinion, the bulk density, not allowing for pores, being far less than unity.

The density of diamond is 3.47–3.56,[15] and that of graphite is 2.25–2.26.[16] Polanyi,[17] like A. M. Williams,[18] considers that the density of active charcoal may be 1.5, and H. Briggs[19] assumes it to be only **1.33,** whereas G. A. Hulett[20] concludes that it is 2.2, approximating that of graphite. The uncertainty arises from the divergent results obtained when the density is determined by immersing the charcoal in different liquids. The values for the density so derived range from 1.65 to 2.28. Two opposing explanations are current for this divergence. The first view is that the liquid sorbed is highly compressed and much denser than the surrounding liquid;

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[14] J. W. McBain, *Nature,* 117,550 (1926), and other communications, *loc. cit.*

[15] "International Critical Tables," Vol. III, 1928, p. 21.

[16] *Ibid.,* Vol. II, 1928, p. 592.

[17] F. Goldmann and M. Polanyi, Z. *physik.* Chem., 132,345 (1928).

[18] A. M. Williams, *Proc. Roy. Soc. Edinburgh,* **38,** 23 (1918); **39,** 48 (1919).

[19] H. Briggs, *Proc. Roy. Soc.* (London), **A100,** 88 (1922).

[20] H. C. Howard and G. *A.* Hulett, J. *Phys. Chem.,* 28,1082 (1924).

hence it would displace less than its own weight of ordinary liquid and, therefore, must add to the apparent density of the charcoal. According to this, the charcoal must be less dense than is ever experimentally observed. The contrary interpretation is that the solid framework of the carbon is of high density, about 2.2, but that, owing to the extreme fineness of its porosity, it is not completely penetrated by liquids. When helium at atmospheric pressure and temperature is used as the fluid displaced by the carbon,[20] the result is unaccompanied by sorption and the density found is 2.2.

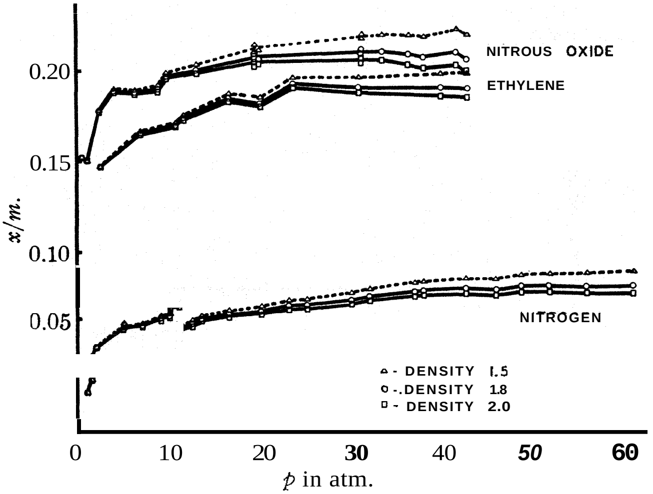

Fig. 8.—Sorption of nitrous oxide, ethylene and nitrogen at 20° assuming the density of charcoal as 1.5, 1.8 and 2.0, respectively. The data used are obtained from Tube III nitrous oxide, Tube III ethylene and Tube I nitrogen.

Although we do not know how completely nitrogen, nitrous oxide and ethylene are able to penetrate the finest porosities of the charcoal, the exact value of the density does not greatly affect the trend of our results. This is illustrated by typical data for all three substances in Fig. 8, which shows what the sorption would be if calculated assuming alternatively the densities 2.0 and 1.8, as well as the inadmissibly low value 1.5. For all three substances it is evident from Fig. 8 that the sorption becomes constant for all the higher pressures, irrespective of whether the density is taken as 1.8 or 2.0. These data, within the experimental error, exhibit a saturation value of sorption.

In Figs. 9, 10 and 11 the values for the sorption are plotted against pressure, being calculated as in the foregoing tables upon the assumed value of 1.8 for the effective density of the charcoal. A saturation value is found for all the experiments with nitrous oxide and ethylene, whereas with nitrogen the saturation value is observed only for the steam-activated charcoal.

However, the uppermost curve in Fig. 11, representing the highest values for sorption by air-activated charcoal at −77°, leads to an almost constant saturation value which would become unmistakable if any higher density were assumed for the charcoal.

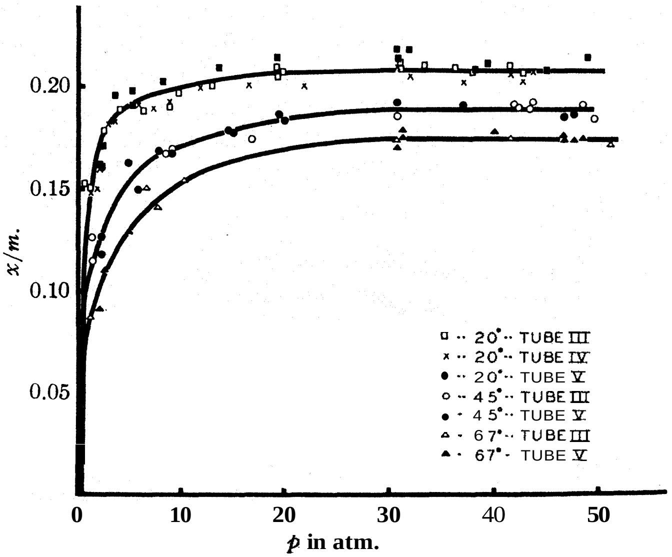

Fig. 9.—Sorption of nitrous oxide by "Steam D" charcoal.

For nitrogen with air-activated charcoal at 20° no saturation value is attained. This is not surprising when we compare the other saturation values corresponding to different temperatures and note that, although they definitely diminish with rising temperature, the highest values for the sorption of nitrogen at 20° are only half those of the corresponding saturation values at −77°. It is evident that appreciably more sorption must take place and much higher pressures must be employed before a saturation value at 20° could be reached.

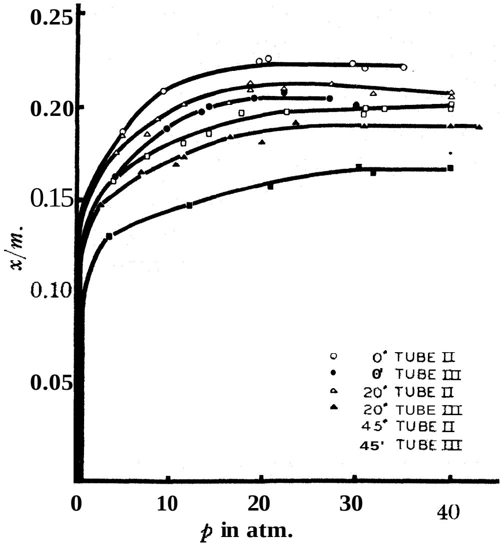

Fig. 10—Sorption of ethylene by "Air C" charcoal.

Data exhibiting a saturation value cannot adequately be represented by the ordinary "exponential" isotherm, $x/m = kp^{1/n}$. Neither can they be represented by the exacting Williams–Henry formula, $\log (x/m/p = k_1 - k_2 \times (x/m)$.

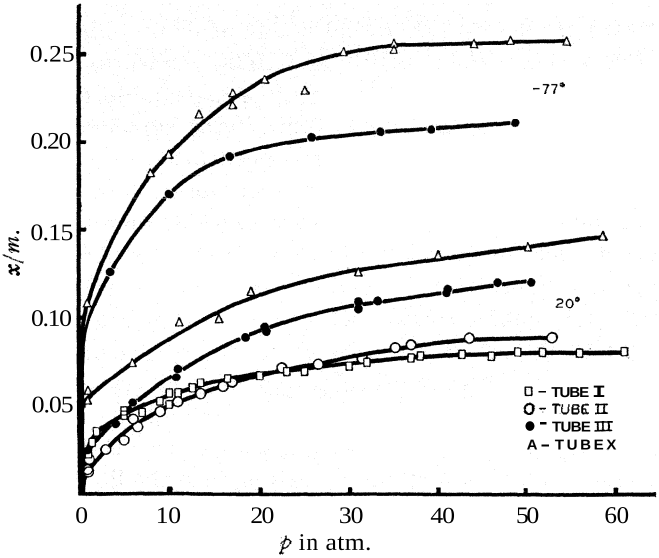

Fig. 11.—Sorption of nitrogen by charcoal. "Steam D" charcoal was used in Tubes I and II, and "Air C" in Tubes III and IV.

This formula cannot be legitimately applied where the sorption exceeds a fraction of the saturation value. The inadequacy of both formulas is illustrated in Figs. 12 and 13, where the respective formulas demand a straight line graph. A saturation value would be indicated by the Williams–Henry graph becoming vertical for that range of pressure. However, over a limited range either formula can be used to give a fair representation of the results.

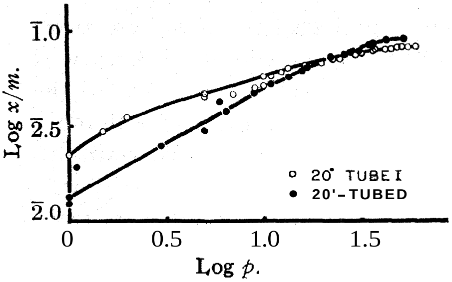

Fig. 12.—Sorption of nitrogen graphed according to the experimental formula, $x/m = kp^{1/n}$.

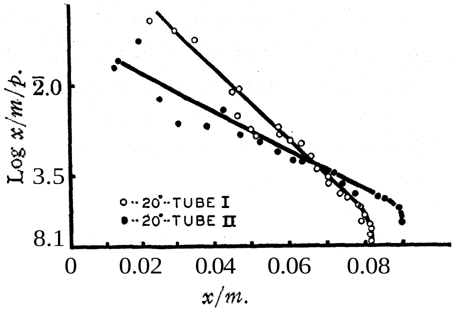

Fig. 13.—Sorption of nitrogen graphed according to the Williams–Henry formula, $\log x/m/p = (k_1 - k_2) \times x/m$.

The question will be raised as to whether some buoyancy correction should not have been introduced for the sorbed gas or vapor itself. The answer is that no such correction is admissible if the classical conception of a compressed film of sorbed material is assumed (de Saussure 1814, Mitscherlich, Bunsen, etc., Polanyi 1917 and 1928). Sorption is defined, both practically and theoretically, as the excess of material in the neighborhood of the solid over that which would obtain if the surrounding atmosphere reached the surface quite unchanged in concentration.

Nevertheless, from the standpoint of chemosorption or of a monomolecular film, it is inevitable that one should seek to distinguish between molecules which are held by sorption and those of the atmosphere which they have displaced. Considering an extreme case such as a body of liquid in contact with a crystalline surface, where the concentration of the liquid is uniform right to the crystal face, by ordinary criteria no sorption would have taken place, yet, if the molecules touching the crystal were specially oriented, they should be regarded as a sorbed monomolecular layer which has displaced an equal bulk of liquid (neglecting here the probable occurrence of oriented chains of molecules reaching into the liquid from a monomolecular layer).[21]

Applying the foregoing considerations to the present cases, the attempt may be made to estimate what the correction would be for the atmosphere displaced by the sorbed material if it is directly attached to the carbon by primary or residual valences. The weight of sorbed material is about one-fifth of that of the carbon, but its volume is uncertain. The densities of solid nitrogen, of liquid nitrogen at −190°, of liquid ethylene at −102° and of nitrous oxide at −89° are 1.0, 0.8, 0.6 and 1.2, respectively. On account of expansion, these densities would be less at the temperatures employed, but this would be partly compensated by compression at the highest pressures. Taking 1.0 and 0.6 as fair limits and assuming for these small molecules that the true density of carbon is 2.2, the combined density of carbon plus sorbed material comes to 1.8 or 1.5. These are equal to the lower densities already considered in Fig. 8 with the important difference that saturation values might still appear with the lower density, owing to the great compressibility which would necessarily accompany so low a density of the sorbed material. The higher density is, moreover, more probable if each sorbed molecule is attached directly to carbon. In other words, the results as portrayed in the graphs are not misleading over the pressure ranges so far investigated even if the actual values might have to be slightly greater and a saturation value was not quite strictly attained. The Langmuir theory supposes that a limiting value for sorption is approached asymptotically with great increase of pressure.

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[21] J. W. McBain and G. P. Davies, THIS JOURNAL, **49**, 2230 (1927); Sir W. Hardy, *J. Gen. Physiol.*, **8**, 641 (1927); J. W. McBain, *Nature*, **120**, 362 (1927).

In Figs. 14, 15 and 16 the results are graphed in a form derived from the Langmuir equation for plane surfaces

$$\frac{x}{m} = \frac{abp}{1 + ap} \text{ or } \frac{p}{x/m} = \frac{1}{ab} + \frac{p}{b}$$

where if a and b are constants, the graphs should be straight lines. It is seen from the figures that this representation is in striking agreement with all the data. When the results for nitrogen at 20° were calculated with alternative densities, it was found that an assumed density of 1.5 did not yield a straight line but that 1.8 was satisfactory and 2.0 was even better. The intercepts of the straight lines with the ordinate on the left of the figures where $p = 0$ give a numerical value of $1/ab$, whereas the slopes of the straight lines give a numerical value of $1/b$.

The results for the sorption of nitrogen at room temperature, extending as they do up to 60 atmospheres pressure, appear to afford the opportunity for a crucial test of the classical de Saussure or Polanyi hypothesis that the sorbed gas is in the form of a compressed atmosphere obeying an ordinary equation of state such as that of van der Waals but under an excess compression due to the attractive forces of the solid. Knowing the actual behavior of nitrogen under compression from the work of Amagat and others, we can consider 1 cc. of the sorption space, that is, the region within which the attractive forces of the solid are operative, and calculate directly what the density of the nitrogen in 1 cc. would be if the average pressure inside the sorption space exceeds that of the surrounding atmosphere by any specified amount.

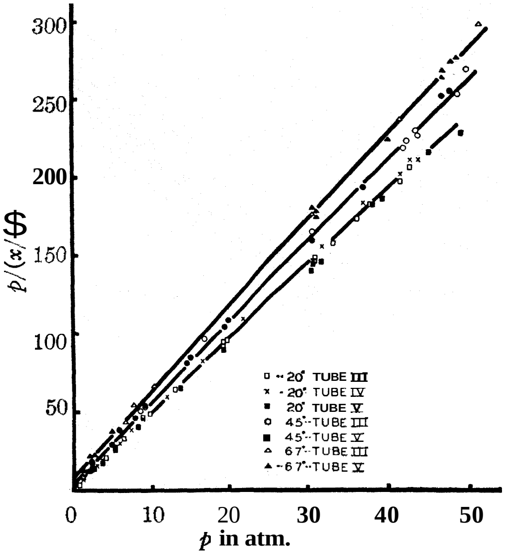

Fig. 14.—Sorption of nitrous oxide by "Steam D" charcoal graphed according to the Langmuir equation, $p/(x/m) = (1/ab) + (p/b)$.

For example, using Amagat's data for values of pv at 16° and various pressures as recorded in "International Critical Tables," the density of nitrogen at 1 atmosphere is 0.00118, and if there is an extra pressure of 1000 atmospheres in the sorption space, the density there would be that corresponding to 1001 atmospheres, namely, 0.5861. The difference in density would be attributed to sorption and would be 0.5849 for a gas pressure of 1 atmosphere. Now if the pressure of the body of the nitrogen were 60 atmospheres, with its density 0.07163, and the excess pressure in the sorption space were again 1000 atmospheres, making a total of 1060 atmospheres, the density then would be 0.5995. Once more the difference in density would be attributed to sorption, and this would amount to 0.5279 for a pressure of 60 atmospheres as compared with the 0.5849 for nitrogen under 1 atmosphere pressure.

In other words, it follows from the known behavior of nitrogen that if nitrogen in the sorption space is like nitrogen in the surrounding atmosphere, except for an extra compression of 1000 atmospheres in the sorption space, we must have observed a distinct decrease in the amount of sorption of nitrogen in our experiments at 60 atmospheres as compared with 1 atmosphere.

Actually, the behavior is wholly different. Instead of the sorption decreasing when the pressure of nitrogen is raised from 1 atmosphere to about 60 atmospheres, the sorption increases many fold. Hence our experiments at high pressures definitely disprove the assumption that the nitrogen in the sorption space is subject to an extra compressive force of the order of 1000 atmospheres.

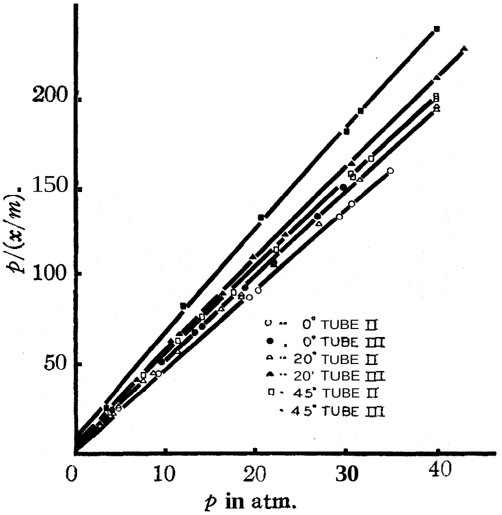

Fig. **15.--Sorption of ethylene by "Air C" charcoal graphed according to the Langmuir equation,** $p/(x/m) = (1/ab) + (p/b)$.

The same test can be applied to a statement that the excess pressure in the sorption space exceeds that in the surrounding space by, say, 100 atmospheres. Here again a slight decrease is predicted in the amount of sorption at the higher pressure, in violent discord with the facts. This apparently conclusive disproof of a conception which has remained up to the present largely a matter of opinion which was held for over a century by almost all the men of science who concerned themselves with this subject, is of such importance that we repeat the experimental data for inspection in tabular form in Table XI to compare with the typical calculations exhibited in Table XII.

It is evident from a comparison of the facts in Table XI with the known behavior of nitrogen in Table XII that they are glaringly incompatible with the conception of a sorption film differing from the surrounding atmosphere merely through compression caused by the attractive forces of the solid. It is clear that of the nitrogen sorbed by charcoal, only a negligible propor-

TABLE XI

SORPTION OF NITROGEN AT 20° OBSERVED AT 1 ATMOSPHERE COMPARED WITH THAT OBSERVED AT A MUCH HIGHER PRESSURE

Tube no	Pressure, atm	x (uncorr.)	x (corr.)	Increase
I	1	0.002084	0.00215	3.5-fold
	61	003636	.00784	
II	1	001063	.00113	7-fold
	53	004656	00812	
III	1	.002255	00233	5-fold
	50.6	.007692	.0114	
IV	1	004897	.00496	2.5-fold
	58.5	008918	.0125	
Wright V′	1.02	.0063	.0066	4-fold
	26.67	.0193	.0264	
Wright VI and VI'	1.02	.0059	.0061	3.5-fold
	31.97	.0152	.0210	

TABLE XII

CALCULATION, FROM AMAGAT'S DATA, OF THE EXCESS CONCENTRATION OR DENSITY OF NITROGEN AT 16° WHICH WOULD OBTAIN AT 1 ATMOSPHERE AS COMPARED WITH 60 ATMOSPHERES IF NITROGEN IN THE SORPTION REGION IS UNDER ANY STATED EXTRA COMPRESSIVE FORCE, *F* ATMOSPHERES. THE DENSITY OF NITROGEN AT 1 ATMOSPHERE IS 0.00118 AND AT 60 ATMOSPHERES IS 0.07163

F, atm.	Density at 1 + *F*	Excess over density at 1 atm.	Density at 60 + F	Excess over density at 60 atm.	Remarks
1000	0.5861	0.5849	0.5995	0.5279	Decrease[a]
100	.1199	.1187	.1849	.1133	Decrease[a]
10	.0130	.01182	.08353	.01190	Very slight increase[a]
5	.0071	00592	.07759	.00596	
1	.0023	.00112	.0729	.00127	

[a] Experiment, on the contrary, shows a many fold increase.

tion can be in the compressed state envisaged in the de Saussure–Polanyi conception, even if this compression be estimated at only 1 atmosphere. Estimates by various advocates of the compressed film theory have ranged up to 37,000 atmospheres.

Clearly the Langmuir conception, which is the only alternative explanation ever put forward for the sorption of nitrogen by charcoal, is correct. Its essence is the assumption that only such molecules are sorbed as are in direct contact with the molecules holding them. The Langmuir conception includes the possibility that further molecules may be held by the primary monomolecular layer.[22] The results and calculations of the present paper disprove, moreover, a further alternative hypothesis introduced by Polanyi

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[22] This view was put forward by R. A. Smith in 1863 (see *Proc.* Roy. *Soc.* (London), **A112,** 301 (1928)). See also, A. B. Lamb, R. E. Wilson, and N. K Chaney, *J. Ind. Eng. Chem.*, 11, 424 (1919); I. Langmuir, *Trans. Faraday Soc.*, 17, 614 (1921); E. K. Rideal [*Nature,* 117, 627 (1926)] who compares such attraction of a magnet on a string of iron filings; F. G. Keyes and M J. Marshall [THIS JOURNAL, 49, 156 (1927)] who especially emphasize it.

in 1928 in an attempt to conform the compressed film concept with monomolecular adsorption by assuming a sideways compression of the adsorbed layer such that it would be the equivalent of a two-dimensional gas or at lower temperatures form islands of liquid.

Experiments with active charcoal do not suffice to disprove the possible existence of relatively weak forces of molecular attraction at distances greater than a molecular diameter. This is due to the extraordinarily complete development of the "porosity" of the charcoal. It must, from such data as ours, be regarded as comparable with that of an open space lattice such as dehydrated chabazite, which acts as a molecular sieve for separating large from small molecules.[23] The sorbed molecules of nitrogen must be so intimately surrounded by the atoms of carbon with which they are in contact that the designation "adsorption," which implies a surface, becomes a misnomer. There is very little difference in such a case between adsorption and absorption;[24] and if a precise word to describe sorption by charcoal were required, the new term "persorption" might be coined. Experiments on smooth surfaces, preferably crystal faces, are required to examine the residual effects which may occur at a greater distance from the surface.

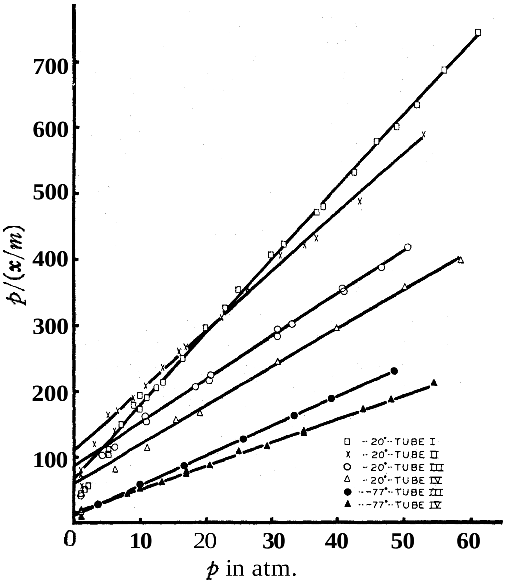

Fig. 16.—Sorption of nitrogen by charcoal graphed according to the Langmuir equation, $p/(x/m) = 1/ab + p/b$. "Steam D" charcoal was used in Tubes I and II, and "Air C" in Tubes III and IV.

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[23] J. W. McBain, *Kolloid-Z.*, 40, 1 (1926); "Colloid Symposium Monograph," Vol. IV, **1926,** p. **7; O.** Weigel and E. Steinhoff, Z. *Krist.*, **61,** 125 (1924); **O.** Schmidt, Ebenda, **133, 263** (1928); R. Seeliger, *Physik. Z.*, **22, 563** (1921); F. Simon, Z. *physik. Chem.*, **132, 456** (1928).

[24] J. W. McBain [*Trans.* Faraday *Soc.*, 14, 202 (1919)] found that in experiments on the sorption of iodine extending over many years, during which the total sorption was doubled, the amounts taken up after the initial sorption conformed with *a* sorption isotherm rather than with a formula for true solution such as Henry's law, although the delay must have been conditioned by slow processes of diffusion. The solvent and other impurities have to diffuse out of the carbon while the solute is diffusing in and replacing them. Modern vacuum technique has not been applied in the study of sorption by solutions.

Although the preceding discussion has been confined to the gas nitrogen as a test case, the result, if recognized as valid, must extend to all cases of sorption by active charcoal.

The critical temperature and pressure of nitrous oxide are 36.5° and 71.7 atmospheres, respectively, those of ethylene 9.7° and 50.9 atmospheres and those of nitrogen −147.1° and **33.5** atmospheres. Nitrogen, therefore, has been studied far above its critical temperature, while nitrous oxide and ethylene have been studied below and above their critical temperatures. The results are all very similar. There is no noticeable influence of this critical constant in the form or position of the sorption curves whether one compares the graphs above and below the critical temperature for one substance or compares the two vapors with nitrogen. This suffices to show that capillary condensation plays no role in such cases of sorption by charcoal.

Summary

1. Using the McBain–Bakr sorption balance, the sorption of nitrogen, nitrous oxide and ethylene has been measured at pressures up to 60 atmospheres.

2. The curves for gases and vapors are similar, and no special difference is noticed when studying nitrous oxide and ethylene above and below their critical temperatures.

3. The data appear to afford a crucial disproof of the classical conception of the sorbed film as a compressed fluid. This was suggested by de Saussure in 1814 and is currently associated with the name of Polanyi. The disproof extends equally to the modification introduced by Polanyi in 1928. The behavior predicted by such hypotheses is in flagrant contradiction with the known compressibility of nitrogen and the actual sorption at 60 atmospheres as compared with that at 1 atmosphere. Only a negligible proportion of the sorbed nitrogen can be in such a state; the remainder must be directly attached as postulated in the hypotheses of Langmuir. It is, therefore, shown that the terms adsorption and absorption are equally misnomers when applied to sorption by active carbon. The dissemination of the sorbed molecules between the carbon atoms is almost as intimate but is not as uniform as that of a true solid solution. On the other hand, owing to so much of the "porosity" of active charcoal being on an atomic or molecular scale, the conception of a surface disappears. The term "persorption" is proposed if a new term is required to describe such phenomena.

4. When the data are expressed according to the definition of Gibbs or of the compressed film conception as the excess in the neighborhood of the surface over the amount corresponding to the surrounding atmosphere, saturation values are obtained for all except some of the experiments with nitrogen. When expressed in absolute amounts, according to the Langmuir conception, the saturation values become doubtful, tending to show slight increase with further rise in pressure.

5. The data over the whole range of higher pressures are adequately represented by the Langmuir formula.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

TWO DELICATE TESTS FOR THE DETECTION OF COPPER AND SOME REMARKS ON THE RHODANINE TEST OF FEIGL FOR SILVER

BY I. M. KOLTHOFF

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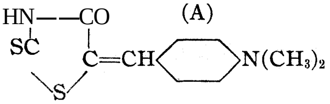
I. Recently, F. Feigl[1] has described a new and very delicate test for silver with *p*-dimethylaminobenzylidene-rhodanine as a reagent (A). According to Feigl, this reagent gives in weakly acid, neutral and ammoniacal solutions, a flocculent red precipitate with silver. In 5 cc. of a weakly acid solution, one part of silver in 5,000,000 of solvent could be detected. In working with 10 cc. of solution, to which 0.5 cc. of 4 N nitric acid and 0.3 cc. of a saturated solution of the rhodanine[2] in alcohol were added, the same sensitivity was found by the writer. A solution with 1 mg. of silver in a liter produces a distinct reddish brown color (10 cc. of solution, conditions as above); with 0.5 mg. of silver per liter a weakly reddish color was noticed; with 0.2 mg. per liter the solution showed a very weak pink color after ten minutes' standing, distinctly different from the blank, which was slightly yellow. In ammoniacal solution (10 cc. of solution +1 cc. of 6 N ammonia and 0.1 cc. of indicator) the color in the presence of silver is reddish-brown and in very dilute solutions orange-brown. The sensitivity in this case is about 2 mg. of silver in a liter.


(A)

In acid medium the reagent is so sensitive toward silver that it even cannot be used as an indicator for the titration of iodide with silver solution. A weakly acid solution of 0.01 N potassium iodide to which some reagent had been added gave a dark red precipitate after addition of a few drops of 0.01 N silver nitrate. Even the silver in the complex potassium silver cyanide reacts with the rhodanine. According to Feigl, the rhodanine is quite specific for silver. This, however, is not the case, as mercury and copper salts under the right conditions can react with it in a very sensitive

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[1] F. Feigl, *Z. anal. Chem.*, 74, 380 (1928).

[2] The reagent was prepared in the organic division of this University, according to the procedure given by Feigl. It had the same properties as a sample kindly submitted by Dr. Feigl. Instead of using a 0.03% solution of the rhodanine in acetone as described by Feigl, a saturated solution in alcohol (about 0.02%) was taken.

way. In weakly acid solution (10 cc. + 0.5 cc. of 4 N nitric acid + 0.3 cc. of reagent) mercurous mercury gives a red precipitate; 1 mg. of mercury per liter gives a faintly red color; the limit of sensitivity is 0.5 mg. per liter. Mercurous mercury even reacts in the presence of chloride; therefore, the rhodanine compound must be less soluble than mercurous chloride. Under the same conditions as described for silver and mercurous mercury, the mercuric mercury in well dissociated mercury salts gives a red color (or precipitate) with the reagent; sensitivity, 0.2 mg. of Hg^{II} per liter (in mercuric nitrate). Addition of chloride or bromide decreases the sensitivity very much. A weakly acid solution of 0.1 N mercuric chloride gives a weak pink color the intensity of which depends upon the acidity of the solution. The reaction cannot be used for a sensitive detection of mercuric nitrate in mercuric chloride. The pink color of the mercuric chloride solution becomes gradually stronger on addition of mercuric nitrate or perchlorate (complex $HgCl^+$ formation).

II. Application of the Rhodanine to the Sensitive Detection of Copper.—With cupric salts the rhodanine produces a reddish-orange color; in stronger solutions a precipitate. A solution of 1 mg. of Cu^{II} per liter gives a brown-orange color which is distinctly different from the yellow color of the blank. If comparison is made with a blank, 0.3 mg. of copper per liter can be detected. It should be mentioned that the formation of the colored product is prevented in acid medium. Even acetic acid decreases the sensitivity greatly. On the other hand, if the copper rhodanine is formed in neutral medium (or in the presence of some excess of sodium bicarbonate) it is fairly stable toward acid. An acid cupric copper solution was neutralized with an excess of sodium bicarbonate, then the reagent was added, whereupon it was acidified with acetic acid. The colors become more pronounced in the acid medium (orange-brown). Bven 0.5 mg. of Cu^{II} per liter can be detected in 5 cc. of solution if a blank treated in the same way is used for comparison. Lead does not interfere.

Cuprous copper gives much more pronounced colors with the reagent A weakly acid solution of cuprous copper containing 100 mg. of Cu^I per liter gives a purple-violet precipitate; 10 mg., red-brown; 1 mg., orange-brown; sensitivity, 0.1 mg. of Cu^I per liter. The rhodanine is very suitable for the detection of traces of copper in a solution. If we start with a cupric copper solution, the divalent ions first must be reduced. This can easily be accomplished with potassium cyanide. To 10 cc. of solution, 3 drops of 1% potassium cyanide and 0.2 cc. of indicator (saturated solution in alcohol) are added and the mixture acidified with acetic acid; sensitivity, 0.3 mg. of copper per liter (comparison with blank). The solution may be acidified with nitric acid instead of acetic acid; 0.5 mg. of copper per liter can be detected easily; the colors fade, however, much sooner than with acetic acid.

Iron interferes with this copper test on account of formation of ferro- or ferricyanide. Therefore, finally, hydrazine sulfate was used as a reagent for the reduction of cupric copper to cuprous copper.

Reagents.—Two per cent hydrazine sulfate; 0 02% rhodanine in alcohol.

Procedure.—To 10 cc. of the solution add a few drops hydrazine sulfate, sufficient 6 N ammonia to give 1 to 2 cc. in excess, 0.2 cc. of rhodanine and acidify, after **five** minutes' standing, with 30% acetic acid. The cuprous copper reacts even in the ammoniacal medium with the indicator; the color is reddish-violet (100 mg. of copper per liter) or orange-brown (10 mg. and less); sensitivity, 0.5 mg. of copper per liter. The colors are more pronounced after acidifying with acetic acid. Even a solution containing 0.3 mg. of copper per liter gives a distinct red-brown color; sensitivity, 0.1 to 0.2 mg. of copper per liter. The blank shows a yellow to brownish-yellow tinge. In order to reach the maximum sensitivity, it is necessary to let the ammoniacal solution stand for five minutes before adding the acetic acid. The reaction is so extremely sensitive that in all samples of distilled water in the laboratory, the presence of 0.2 to 0.4 mg. of copper per liter could be shown. In the experiments described in this paper, conductivity water or redistilled water from glass vessels was used as a solvent. Water thus obtained gave a negative test for copper. The reaction according to the above procedure is very suitable for the detection of copper in the presence of other cations (silver and mercury excepted). One part of copper in the presence of 2000 parts of lead, bismuth, cadmium, nickel, cobalt and manganese, respectively, could be detected easily. The precipitate formed in the presence of lead or bismuth does not interfere.

Traces of iron do not interfere. Larger amounts can be made harmless by acidifying the ammoniacal solution with phosphoric acid instead of acetic acid. The hydrous ferric oxide goes into solution as colorless complex ferric phosphate. A solution containing 1 mg. of copper and 100 mg. of ferric iron in a liter gave a distinct test for copper. It should be mentioned that the color of the cuprous compound of rhodanine is less stable in phosphoric acid than in acetic acid. It seems that the reaction according to the general procedure is very suitable for the detection of traces of copper in distilled and tap water. The copper content can be approximated by using solutions of known content for comparison.

After this work was finished, an abstract of a paper of O. Funakoshi[3] appeared in *Chemical Abstracts.* It is only stated there that cuprous copper gives a reddish-violet precipitate with rhodanine at about the same sensitivity in neutral or slightly acid solutions. Colors are obtained with concentrated solutions of cupric copper, but the products are much more soluble in water.

III. Recently S. G. Clarke and B. Jones[4] published a note concerning a new and very sensitive reaction for copper. The solution, which must be free from chloride, is neutralized and rendered faintly acid (1 drop of dilute sulfuric acid in excess) and placed in a 100-cc. Nessler glass. One gram of ammonium persulfate is dissolved in the solution; 1 cc. of a saturated alcoholic solution of dimethylglyoxime, 0.5 cc. of 0.5% silver nitrate and 2% of a 10% aqueous solution of pyridine are added and the whole stirred. Copper gives a reddish-violet color. The reaction is quite specific and sensitive to 0.1 mg. of copper in a liter. The author was able to confirm more or less the statements of Clarke and Jones. In working with 10 cc. of solution a sensitivity of 0.3 mg. of copper in a liter was noticed. **A** serious

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[3] Funakoshi, Mem. *Coll. Sci., Kyoto Imp. Univ., 12,* 155 (1929); C. *A., 23, 4644* (1929).

[4] S. G. Clarke and B. Jones, *Analyst,* 54, 333 (1929).

drawback is that chloride must be absent, which limits the application of the reaction very much. Therefore, it was thought worth while to make a search for another oxidizing agent instead of persulfate. Potassium periodate[6] was found to be very suitable. The high price of this salt is no objection, as for each experiment only 4 mg. of potassium periodate are used. A systematic study showed that the amount of periodate and dimethylglyoxime have a marked influence upon the sensitivity of the reaction. In the presence of much periodate, the red color of the copper compound fades fairly rapidly. The periodate probably oxidizes the glyoxime to some product which gives the red color with copper. An excess of periodate oxidizes this compound further to a colorless product. This could be inferred from the fact that if some dimethylglyoxime was added to *a* solution which had become colorless on standing, the red color developed again. It would be interesting to know the composition of the compound which gives the red color with copper. If this oxidation product of dimethylglyoxime could be isolated, it might be expected that it would be a valuable reagent for the detection of traces of copper.

Finally, the following procedure was developed for the detection of traces of copper in distilled water.

Reagents.—Saturated solution of potassium periodate in water (0.35 g. of the salt in 100 cc. of water); 0.1% dimethylglyoxime in alcohol (the saturated solution which Clarke and Jones used contains about 1.6 g. of glyoxime in 100 g. of alcohol and is much too concentrated for our purpose). It may be mentioned that an old solution of dimethylglyoxime which had been kept for some years in an ordinary bottle gave a much less sensitive reaction. The reason was that the solution had become strongly alkaline to phenolphthalein.

Procedure.—To 10 cc. of water add 0.2 to 0.3 cc. of 0.1% dimethylglyoxime and 1 cc. of saturated potassium periodate solution. Observe the color after three to five minutes' standing. A violet-red color shows the presence of copper; sensitivity: 0.1 mg. of copper in a liter ($1:10^7$).

Notes.—(1) It makes no difference whether the dimethylglyoxime or the periodate is added first. In order to avoid confusion with nickel, it is advisable to add the dimethylglyoxime first. (2) The red-violet color develops gradually and attains a maximum sensitivity after about five minutes' standing. After long standing, the color fades. Still the procedure described can be applied for the colorimetric determination of traces of copper in distilled water if comparisons are made within fifteen minutes after addition of the reagents. In this way it was found that distilled water in this Laboratory contained 0.2 to 0.4 mg. of copper in a liter. (3) In working with a larger volume than 10 cc., even smaller amounts than 0.1 mg. of copper in a liter can be detected. (4) Small amounts of alkali chlorides and other neutral alkali salts have no influence upon the reaction. Small amounts of sodium bicarbonate (less than 1 g. in a liter) have no influence; with larger amounts the sensitivity decreases somewhat, but even in the presence of 10 *g.* of sodium bicarbonate per liter, 1 mg. of copper in a liter could be detected easily. (5) Calcium and magnesium, especially in the presence of bicarbonate

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[6] Potassium periodate has been applied for the oxidation of manganese to permanganate. Compare especially H. H. Willard and L. H. Greathouse, **This** JOURNAL, **39,** 2366 (1917).

(tap water) interfere, as they precipitate with the periodate. This difficulty can be overcome by adding to 10 cc. of water 1 cc. of 4 *N* sulfuric acid and 50 mg. of sodium bicarbonate. In this way it could be shown that the Minneapolis tap water contains less than 0.1 mg. of copper in a liter. It is still more convenient to add a buffer solution to the water instead of the combination of sulfuric acid and bicarbonate. The more acid the solution the less sensitive is the reaction. Finally, it was found that with an acetate buffer of PH 5.8 * 0.2, good results are obtained.

Acetate Buffer.—One hundred cc. of N sodium acetate and 7 cc. of N acetic acid.

Procedure.—To 10 cc. of water, 1 cc. of buffer solution is added and then the glyoxime and the periodate as described above; the sensitivity after standing for five minutes is 0.15 mg. of copper in a liter.

The latter procedure can be applied for the detection of copper in tap water if not more than traces of zinc or lead are present; 10 mg. of zinc in a liter has very little influence (color somewhat weaker than in blank without zinc); in the presence of larger amounts of zinc, the latter is precipitated as zinc periodate and the sensitivity decreases very much. The same holds for lead. A solution with 1 mg. of copper in a liter in the presence of 10 mg. of lead per liter gives a distinct reaction though a somewhat weaker color than without lead. Ferric iron also interferes. Still 1 mg. of copper per liter in the presence of 10 mg. of iron per liter gives a distinct reaction. Addition of 1 to 2 drops of N disodium phosphate (Na_2HPO_4) before the addition of the buffer gives a great improvement. Under these conditions 1 mg. of copper in the presence of 20 mg. of iron per liter can easily be detected. Other cations such as cadmium, zinc or manganese all interfere, as they precipitate with the periodate. Therefore, the rhodanine reaction is of much more general application than the glyoxime reaction. The latter can only be applied in these cases in which the solution does not contain more than traces of other metal salts.

Summary

1. *p*-Dimethylaminobenzylidene-rhodanine is a sensitive reagent for the detection of mercurous mercury and mercuric ions. Slightly ionized mercuric salts produce only a slight color or none.

2. Salts of cupric copper give an orange-reddish or orange-brown color. The latter is more pronounced in cuprous salts. A delicate and simple test based on this reaction and sensitive to 0.1 mg. of copper in a liter has been described. The reaction is very suitable for the detection of copper in distilled water, tap water and in solutions which contain other metal ions.

3. The reaction of Clarke and Jones for copper, using dimethylglyoxime and persulfate plus silver nitrate, has been modified by using a trace of periodate as an oxidizing agent. The reaction is sensitive to 0.1 mg. of copper in a liter and is very useful for the colorimetric determination of traces of copper in distilled water. A somewhat modified procedure has been described for the detection of copper in tap water. The rhodanine test can be more generally applied than the dimethylglyoxime reaction.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. IX. THE ELECTRIC MOMENTS OF THE ALKYL HALIDES AND HALOGENATED METHANES

BY C. P. SMYTH AND H. E. ROGERS

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The electric moments of butyl chloride, bromide and iodide and heptyl bromide have been determined with a view to ascertaining the effect of the length of the hydrocarbon chain upon the moment of the molecule and to observing whether the variation from chloride to bromide to iodide is the same in large molecules as in small. At the same time it is possible to study the dependence of the mutual orienting effects of the molecules upon molecular size. The previously unmeasured bromine and iodine substituted methanes have been investigated in order to throw further light upon the mutual repulsion of atoms or groups in the same molecule,

Method of Measurement

The methods of measurement and calculation used in the present work have been described in the first two papers of the series[1] on dielectric polarization, and a subsequently developed cell with four different fixed capacities, which was used in some of the measurements, has been described in a later paper. The dielectric constants[2] were measured with the capacity bridge originally used, a frequency of 5×10^5 cycles, corresponding to a wave length of 600 meters, being employed as before. The errors were similar to those described in the last mentioned paper, dielectric constant values below 5 having a probable error of 0.2% and those above 5 having a probable error of 0.5%. The relative error within a given series of measurements was much smaller in both cases. Since the same type of pycnometer was used as in the earlier work, the probable error in the densities was the same, being about 0.07% in the low temperature determinations and not more than 0.03% in the measurements above 0°.

Preparation of Materials

Heptane.—Pure normal heptane was obtained from the Ethyl Gasoline Corporation. As the boiling point, refractive index, and dielectric constant of a sample were not appreciably different after washing with sulfuric acid, followed by sodium carbonate solution and water, drying over calcium chloride and finally distilling over sodium, the heptane was used without purification.

Benzene.—Merck's C. P. benzene was washed three times with concentrated sulfuric acid, followed by dilute sodium hydroxide solution and water, dried over calcium chloride and crystallized twice; m. p. 5.47°. It was then allowed to stand over sodium and distilled from it; b. p. 80.1°; n_D^{20} 1.50135.

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[1] Smyth, Morgan and Boyce, THIS JOURNAL, **50,** 1536 (1928); Smyth and Morgan, *ibid.*, **50,** 1547 (1928).

[2] Smyth and Stoops, ibid., **51,** 3312 (1929).

Butyl Chloride.—*n*-Butyl chloride obtained from the Eastman Kodak Company was refluxed gently with concentrated sulfuric acid, distilled, washed with water, dried over calcium chloride and distilled; b. p. 77.5"; n_D^{20} 1.40148.

Butyl Bromide.—n-Butyl bromide obtained from the Eastman Kodak Company was washed with cold concentrated sulfuric acid, then with sodium carbonate solution, dried over calcium chloride and distilled; b. p. 101.0°; n_D^{20} 1.43985.

Butyl Iodide.—*n*-Butyl iodide obtained from the Eastman Kodak Company was shaken once with ice-cold concentrated sulfuric acid and eight times with dilute sodium hydroxide, washed with water, dried over calcium chloride and distilled at reduced pressure; d_4^{20} 1.616.

Heptyl Bromide.—*n*-Heptyl bromide obtained from the Eastman Kodak Company was washed with cold concentrated sulfuric acid, sodium carbonate solution, and water, dried over calcium chloride and distilled at reduced pressure. A fraction boiling within a 0.2" interval was taken; d_4^{16} 1.144; n_D^{20} 1.44972. "International Critical Tables" give d_4^{16} 1.133, in good agreement with the value d_4^{16} 1.134 obtained for the unpurified material. The purified material was treated again in the same way and the product obtained had the same density as before, d_4^{16} 1.144. This was, therefore, concluded to be the correct value for the pure material.

Methylene Bromide.—Material obtained from the Eastman Kodak Company was washed with dilute sodium carbonate solution and water, dried over calcium chloride and distilled at reduced pressure; d_4^{20} 2.4921; n_D^{20} 1.53559.

Methylene Iodide.—Kahlbaum's methylene iodide was washed with dilute sodium hydroxide solution and water, dried over calcium chloride and distilled at reduced pressure; d_4^{25} 3.3104.

Bromoform.—Material obtained from the Eastman Kodak Company was washed with concentrated sulfuric acid, followed by dilute sodium hydroxide solution and water, dried over anhydrous potassium carbonate and distilled at reduced pressure; d_4^{20} 2.889.

Iodoform.—Kahlbaum's iodoform, which melted at 119.0°, was used without purification.

Experimental Results

The densities, which showed but slight departure from a linear dependence upon temperature, were determined at approximately 25° intervals and the dielectric constants at 15° intervals. The majority of the densities, d, and dielectric constants, ϵ, in Table I were obtained at 10° intervals by graphical interpolation, and the polarizations, P_2, of the polar components were calculated from them by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{c_1M_1 + c_2M_2}{d} \text{ and } P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2, and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. The solutions of methylene bromide, methylene iodide and bromoform were measured at the same two or three fixed temperatures and, therefore, require no interpolation to make them comparable.

Discussion of Results

When the P_2–c_2 curves are extrapolated to $c_2 = 0$, the values of P obtained, designated as P_∞, give a straight line when multiplied by T and

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AND POLARIZATIONS OF POLAR COMPONENTS

Heptane–Butyl Chloride

Mole fr. of C_4H_9Cl = t, °C.	0	0.0242	0.0653	0.0889	0.1562	0.2191	0.2617	0.5619	0.8623	1.000
−90	2.083	2.219	2.440	2.567	2.954	3.359	3.659	6.302	10.16	12.24
−70	2.055	2.175	2.376	2.485	2.837	3.184	3.453	5.792	9.228	10.98
−50	2.027	2.135	2.315	2.413	2.732	3.038	3.266	5.322	8.465	9.940
−30	1.999	2.096	2.259	2.347	2.635	2.904	3.122	4.924	7.743	9.073
−10	1.972	2.058	2.206	2.285	2.547	2.792	2.986	4.586	7.077	8.320
10	1.944	2.022	2.157	2.227	2.466	2.688	2.861	4.285	6.518	7.663
30	1.916	1.985	2.108	2.174	2.393	2.591	2.745	4.025	6.062	7.090
50	1.888	1.950	2.059	2.122	2.319	2.494	2.642	3.792	5.676	6.558
70	1.858	1.913	2.007	2.070	2.248	2.410	2.543	3.570	5.250	6.045
						d				
−90	0.7752	0.7778	0.7836	0.7864	0.7993	0.8025	0.8205	0.8820	0.9618	1.0050
−70	.7587	.7613	.7678	.7700	.7826	.7872	.8029	.8630	.9400	.9794
−50	.7420	.7448	.7513	.7539	.7659	.7718	.7853	.8438	.9191	.9580
−30	.7252	.7280	.7347	.7375	.7488	.7561	.7673	.8247	.8980	.9375
−10	.7088	.7114	.7181	.7209	.7317	.7402	.7490	.8057	.8769	.9157
10	.6921	.6947	.7011	.7043	.7148	.7243	.7313	.7867	.8559	.8950
30	.6755	.6775	.6843	.6878	.6975	.7070	.7130	.7675	.8355	.8736
50	.6576	.6606	.6668	.6708	.6790	.6889	.6949	.7475	.8148	.8513
70	.6392	.6428	.6486	.6528	.6603	.6708	.6759	.7271	.7925	.8275
						$P_2(C_4H_9Cl)$				
−90	157.7	153.2	141.2	137.1	127.5	124.5	118.1	96.76	79.52	72.68
−70	146.5	143.6	133.7	129.4	122.0	118.1	113.3	94.82	79.12	70.98
−50	136.5	134.6	126.3	122.5	116.8	112.7	108.4	92.50	78.72	72.32
−30	128.5	126.5	120.2	116.7	112.1	107.9	105.2	90.34	78.12	71.96
−10	121.7	120.7	114.6	111.3	107.9	103.9	102.0	88.30	77.33	71.67
10	116.1	115.0	110.1	106.3	103.8	101.1	98.62	86.32	76.60	71.29
30	111.3	109.6	105.4	102.4	100.8	97.73	95.64	84.57	76.02	70.96
50	106.6	101.5	99.10	97.44	97.01	94.35	92.75	82.88	75.58	70.59
70	102.4	94.48	92.42	93.45	93.61	90.02	90.13	81.04	74.70	70.12

Heptane–Butyl Bromide

Mole fr. of C_4H_9Br = t, °C.	0.0456	0.0930	0.1409	0.2579	0.4154	0.5959	0.8413	1.000
					ε			
−90	2 349	2.588	2.854	3.548	4.687	6.280	8.970	11.08
−70	2.289	2.513	2.751	3.379	4.389	5.810	8.220	10.14
−50	2.239	2.441	2.653	3.226	4.119	5.405	7.565	9.258
−30	2.193	2.373	2.568	3.086	3.886	5.044	6.984	8.520
−10	2.149	2.310	2.491	2.957	3.679	4.732	6.474	7.880
10	2.107	2.251	2.417	2.843	3.499	4.454	6.039	7.315
30	2.064	2.197	2.346	2.737	3.336	4.203	5.640	6.799
50	2.022	2.146	2.279	2.640	3.187	3.966	5.290	6.345
70	1.979	2.097	2.217	2.547	3.050	3.761	4.969	5.930
90	1.938	2.049	2.158	2.455	2.914	3.577	4.662	5.535

TABLE I (*Continued*)

Mole fr. of C_4H_9Br = t, °C.	0.0456	0.0930	0.1409	0.2579	0.4154	0.5959	0.8413	1.000
	d							
−90	0.7960	0.8195	0.8432	0.9072	0.9986	1.1152	1.2967	1.4310
−70	.7783	.8022	.8260	.8884	.9781	1.0927	1.2708	1.4040
−50	.7616	.7849	.8087	.8694	.9575	1.0698	1.2449	1.3735
−30	.7456	.7679	.7913	.8505	.9372	1.0472	1.2188	1.3450
−10	.7295	.7510	.7740	.8318	.9170	1.0245	1.1926	1.3170
10	.7125	.7337	.7560	.8127	.8964	1.0017	1.1663	1.2880
30	.6949	.7159	.7375	.7931	.8750	.9780	1.1397	1.2592
50	.6775	.6977	.7183	.7723	.8528	.9542	1.1129	1.2300
70	.6589	.6786	.6993	.7514	.8307	.9298	1.0853	1.2005
90	.6397	.6590	.6803	.7306	.8073	.9043	1.0562	1.1695

	P_∞	$P_2(C_4H_9Br)$							
−90	157.8	153.2	136.3	129.7	118.6	105.2	94.2	80.9	73.8
−70	146.5	144.4	130.9	124.2	114.7	102.4	92.2	80.2	73.5
−50	138.6	136.2	124.7	118.5	111.0	99.53	90.6	79.4	73.2
−30	131.7	129.7	118.9	113.9	107.5	96.88	88.9	78.7	72.8
−10	124.2	124.1	113.4	110.6	104.0	94.35	87.0	77.9	72.4
10	118.6	119.3	109.2	106.1	100.9	92.18	86.0	77.2	72.1
30	113.4	115.1	105.7	102.1	98.02	90.28	84.7	76.5	71.7
50	109.2	109.3	101.9	98.94	95.85	88.46	83.2	75.9	71.3
70	106.2	104.5	99.57	95.81	93.56	86.77	82.0	75.2	70.9
90	103.0	102.9	98.34	93.84	91.21	85.13	81.1	74.6	70.5

Heptane–Butyl Iodide

Mole fr. of C_4H_9I = t, °C.	0.0386	0.0831	0.1698	0.2943	0.5462	0.8090	1.000
	ϵ						
−80	2.247	2.450	2.862	3.529	5.044	7.085	8.890
−60	2.201	2.386	2.760	3.351	4.729	6.543	8.180
−40	2.157	2.325	2.668	3.195	4.445	6.082	7.534
−20	2.115	2.271	2.585	3.063	4.188	5.673	7.002
0	2.076	2.219	2.506	2.939	3.971	5.304	6.542
20	2.038	2.169	2.432	2.820	3.783	5.005	6.117
40	2.001	2.119	2.360	2.718	3.614	4.755	5.737
60	1.964	2.073	2.295	2.630	3.465	4.507	5.421
80	1.925	2.027	2.229	2.556	3.318	4.254	5.108
	d						
−80	0.7993	0.8352	0.9082	1.0221	1.2619	1.5497	1.7842
−60	.7818	.8172	.8892	.9993	1.2361	1.5187	1.7505
−40	.7644	.7992	.8702	.9771	1.2109	1.4883	1.7168
−20	.7470	.7810	.8509	.9549	1.1854	1.4582	1.6832
0	.7296	.7628	.8314	.9329	1.1596	1.4278	1.6495
20	.7118	.7446	.8112	.9111	1.1339	1.3976	1.6158
40	.6940	.7263	.7912	.8900	1.1079	1.3674	1.5824
60	.6757	.7075	.7711	.8675	1.0816	1.3369	1.5485
80	.6571	.6885	.7505	.8449	1.0551	1.3063	1.5144

TABLE I *(Continued)*

t, °C.	Mole fr. of C_4H_9I = P_∞	0 0386	0 0831	0 1698	0 2943	0.5462	0 8090	1 000
		$P_2(C_4H_9I)$						
−80	136.6	137 6	124 6	116 4	107.6	93 1	81 7	74 6
−60	1271	1230	119.0	1119	1040	912	806	741
−40	1209	1163	1140	1082	1008	89.1	796	735
−20	1154	1112	1101	1048	982	87.4	786	729
0	111 1	107 1	106 3	101 6	95 5	85 9	77 5	72 4
20	107.6	1044	1031	989	927	846	768	718
40	103 0	100 3	99 0	95 8	90 2	83 4	76 2	71 1
60	98 4	96 7	95 9	93 2	88 7	82 5	75 5	70 8
80	95 6	92 9	93 1	90 5	87 9	81 4	74 5	70 2

Heptane–Heptyl Bromide

t, °C.	Mole fr. of $C_7H_{15}Br$ =	0 0488	0.0889	0 1626	0 3330	0 5327	1.000
−70		2297	2.491	2862	3704	4809	7.385
−50		2 247	2.422	2 755	3 515	4 498	6 875
−30		2 198	2.356	2 656	3 348	4 214	6 392
−10		2.152	2.294	2 567	3.200	3 969	5 957
10		2 109	2 237	2 489	3 067	3 767	5 582
30		2 067	2 184	2 417	2 950	3 595	5 255
50		2 024	2 133	2 349	2 840	3 437	4 970
70		1 980	2 083	2 278	2 734	3 284	4 711
90		1 936	2.033	2 210	2 632	3.134	4 476
		d					
−70		0 7831	0 8039	0 8428	0 9348	1.0243	1 2370
−50		.7667	.7871	.8249	9166	1 0044	1 2160
−30		.7502	.7702	8075	.8981	.9849	1.1944
−10		.7333	.7533	7895	.8793	.9657	1 1725
10		.7165	.7359	.7712	.8606	.9456	1.1507
30		.6988	.7184	.7534	.8420	.9255	1 1285
50		.6810	.7004	.7354	.8227	.9056	1.1065
70		.6632	.6821	.7171	.8032	.8858	1 0847
90		.6442	.6633	.6978	.7836	.8648	1 0622
	P_∞	$P_2(C_7H_{15}Br)$					
−70	...	152 3	146.1	139 0	123.8	115 7	98 5
−50	149 6	145 3	139 7	133 6	119.9	112 8	97 5
−30	141 6	138.4	133.7	128 4	116.5	109 9	96.3
−10	1346	1327	128.0	124.0	113.4	107.1	951
10	128 3	127 7	123 3	120 5	110 6	105 0	94 0
30	125.5	124.4	119.6	117.3	108 2	103 4	93.0
50	...	118.2	115.2	113 9	105.7	101 6	92 1
70	...	112 1	111 6	109 9	103.3	99 7	91 3
90	...	108.4	108.8	106.9	101.0	97.0	90 5

Benzene–Methylene Bromide

t, °C.	Mole fr. of CH_2Br_2 = 0.0496	0 0947	0.2038	0 5618	0 8114	1 000
10	2 460	2 596	2 957	4 420	5 884	7 772
40	2 383	2 502	2 815	4 088	5 335	6 678
70	2 293	2 401	2 676	3 841	4 848	

TABLE I (*Continued*)

t, °C.	Mole fr. of CH_2Br_2 =	0 0496	0.0947	0.2038	0.5618	0 8114	1.000
		d					
10		0.9530	1.0117	1.1607	1.7015	2.1418	2.5438
40		.9192	.9759	1.1202	1.6463	2.0734	2.4442
70		.8844	.9395	1.0795	1.5984	2.0042	
	P_∞	$P_2(CH_2Br_2)$					
10	64.4	62.4	60.8	58.6	52.7	49.3	47.1
40	62.1	60.1	58.5	56.5	51.4	48.5	46.5
70	59.0	56.9	56.5	54.7	50.6	47.6	

Benzene–Methylene Iodide

t, °C.	Mole fr. of CH_2I_2 =	0 0268	0 0449	0 0636	0 1337	0 1943	1.000
25		2341	2.384	2425	2592	2734	5316
50		2 282	2.322	2.359	2 524	2 646	
		d					
25		0.9330	0.9721	1.0137	1.1728	1.3065	3.3105
50		.9045	.9432	0.9832	1.1351	1.2706	
	P_∞	$P_2(CH_2I_2)$					
25	56.3	54.4	56.2	55.7	55.1	56.1	47.74
50	54.6	52.2	54.2	54.2	55.6	53.0	

Benzene–Bromoform

1, °C.	Mole fr. of $CHBr_3$ =	0.0409	0.0573	0.0718	0.0929	0.2340	0.5047	0.7358	7.000
10		2.308	2.411	2.438	2.477	2.726	3.232	3.726	4.404
40		2.315	2.340	2.365	2.399	2.623	3.075	3.506	4.084
70		2.234	2.258	2.284	2.313	2.522	2.924	3.315	3.816
		d							
10		0.9711	1.0045	1.0330	1.0751	1.3591	1.9068	2.3818	2.9189
40		.9366	.9689	.9969	1.0380	1.3144	1.8487	2.3134	2.8383
70		.8997	.9333	.9603	1.0004	1.2692	1.7898	2.2446	2.7597
	P_∞	$P_2(CHBr_3)$							
10	51.0	48.5	50.8	50.1	50.4	49.1	47.5	46.6	46.05
40	49.9	48.6	49.1	49.2	49.1	48.0	46.6	45.6	45.17
70	48.5	45.0	47.3	46.8	46.8	46.9	45.6	44.9	44.37

Benzene–Iodoform

Mole fr. of CHI_3 = t, °C.	0	0.0063	0.0222	0.0352	0	0.0063	0.0222	0.0352
10	2.315	2.323	2.361	2.387	0.8896	0.9096	0.9663	1.0100
20	2.295	2.307	2.341	2.366	.8786	.8991	.9550	.9989
30	2.274	2.291	2.321	2.345	.8682	.8880	.9436	.9869
40	2.253	2.272	2.298	2.322	.8574	.8768	.9322	.9750
50	2.232	2.252	2.275	2.299	.8466	.8657	.9210	.9631
60	2.210	2.230	2.250	2.274	.8357	.8546	.9096	.9512
70	2.188	2.206	2.226	2.248	.8246	.8434	.8979	.9392

TABLE I (Concluded)

t, °C.	Mole fr. of CHI_3 = P_∞	0.0063	0.0222 $P_2(CHI_3)$	0.0352
10	...	56.5	59.6	53.5
20	61.5	63.6	60.1	59.5
30	...	66.8	61.0	60.1
40	...	73.2	60.1	59.5
50	59.6	87.6	58.8	59.0
60	...	87.6	57.0	58.1
70	...	84.4	55.7	56.4

plotted against T (Fig. 1), as required by the Debye equation: $P = a + b/T$, in which $a = P_E + P_A$, the sum of the electronic polarization, P_E, and the atomic, P_A, and $b = 4aNp^2/9k$, N being the Avogadro number, **6.061** X 10^{23}, μ, the electric moment, and k, the molecular gas constant, **1.372** X 10^{-16}. When the equation is written in the form $(P, - a)T = b$, it is evident that it can be tested by the constancy of $(P, - a)T$, the values of which are given in Table II.

TABLE II

VALUES OF $(P, - a)T$

T, °A.	$(P_\infty - a)T$ C_4H_9Cl	 C_4H_9Br	 C_4H_9I	 $C_7H_{15}Br$
183	21810	20290	...	
193	21920	20270	15900	...
203	21920	20220	16180	...
213	21940	20380	15530	20510
223	21850	20450	15500	20590
233	21800	20130	15540	20780
243	21870	20610	15650	20630
253	21960	20420	15480	20440
263	21880	20330	15520	20490
273	22170	20280	15530	20310
283	21960	20280	15730	20260
293	21920	20330	15650	20690
303	22060	20150	15630	20850
313	21910	20410	15270	20630
323	22000	20120	14660	...
333	21910	20280	15060	...
343	21920	20340	14750	
353	...	20400	14620	

In the case of butyl iodide, a small decrease in the values of $(P, - a)T$ accompanies rising temperature at the higher temperatures, probably because of slight decomposition of the substance. Below 30° for the butyl iodide and over the entire temperature range within which the other substances are liquid, the values of $(P, - a)T$ are constant, giving further proof, if further proof is needed, of the applicability of the Debye equation to polar liquids highly diluted by non-polar.

The best values of *a* and b were obtained from the curves in Fig. 1 and the electric moments were then calculated from b. The values of P_E at infinite wave length were calculated from the molar refractions given in Landolt–Börnstein (5th ed.) by means of the equation, $P_E = [1 - \lambda_0^2/\lambda^2][(n^2 - 1)M/(n^2 + 2)d]$, in which *n* is the refractive index for light of wave length λ, λ_0 is the wave length corresponding to a characteristic vibration frequency in the ultraviolet region, and *d* is the density. As dispersion data were not available for heptyl bromide, the value of P_E at infinite wave length was estimated by subtracting 1.0, a difference analogous to those found for the other halides, from 42.20, the molar refraction for the sodium D-line. The result, 41.2, should be within 0.3 of the correct value. The atomic polarization, P_A, has been obtained by subtracting P_E'from *a*. The results are shown in Table III.

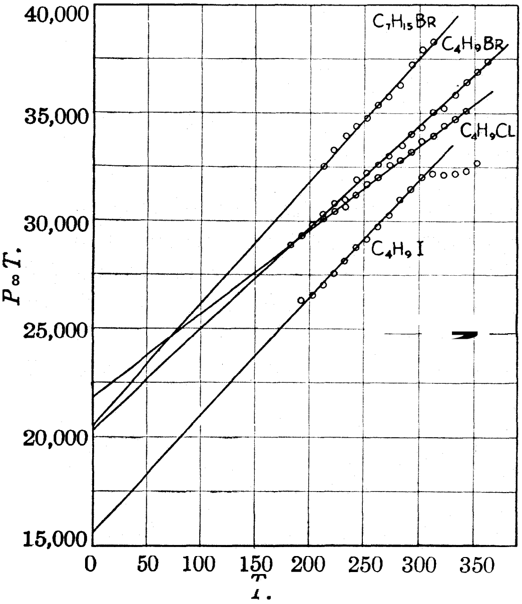

Fig. 1.—Variation of $P_\infty T$ with *T*.

TABLE III

VALUES OF FUNDAMENTAL CONSTANTS

	a	P_E	P_A	*b*	$\mu \times 10^{18}$
C_4H_9Cl	38.5	24.9	13.6	21920	1.88
C_4H_9Br	46.9	27.6	19.3	20300	1.81
C_4H_9I	54.2	32.3	21.9	15530	1.59
$C_7H_{15}Br$	56.7	41.2	15.5	20610	1.83

The values of P_A are surprisingly high and may be considerably in error, as a small change in the curve has a large effect upon *a* and, consequently, an even greater effect upon the difference, $a - P_E$, but the accuracy of the curves is such as to render a small P_A for these substances highly improbable. Moreover, a value of 12.3 has been determined with some accuracy for ethyl iodide[2] and a rough value of 11 has been found for ethyl bromide.[1] Preliminary measurements carried out in this Laboratory upon heptyl bromide in the solid state indicate a value for P_A of the same order of magnitude as that here found. In the butyl halides, the values increase from chloride to bromide to iodide, but, in view of the uncertainty of the values, great significance cannot be attached to this.

The substituted methanes were measured over too limited a range of temperature to permit of an accurate determination of a and b by plotting P_∞ against $1/T$. As is very commonly done, a was assumed equal to MR_D, the molar refraction for the D-sodium line, and the electric moment was calculated from $P_\infty - MR_D$. The values of MR_D for methylene bromide and bromoform were taken directly from Landolt–Börnstein (5th ed.), while those for methylene iodide and iodoform were calculated as the sum of the atomic refractions, the accuracy of the values thus obtained being quite sufficient for the purpose. Values of the electric moments calculated at different temperatures showed very close agreement except in the case of iodoform, the results for which are less accurate than the others because of its low solubility and decomposition in solution. The small values of the difference $P_\infty - MR_D$ for this substance increase the relative error of the moment. At 20° the value obtained was 0.84×10^{-18}, and at 70°, 0.77×10^{-18}. The necessary neglect of P_A in calculating this moment causes the mean value 0.8×10^{-18} given in Table IV to be too high. Indeed, if iodoform had a value of P_A comparable to those given in Table III, its moment would be zero. It seems probable that the true value of the moment of iodoform is little more than half the value given in Table IV, while the values for methylene bromide and iodide and bromoform are also a little high because of neglect of P_A, which, however, affects these moments less than that of iodoform because of their higher values. As most investigators have neglected P_A[3] in calculating the moment, it seems best, for the sake of comparison, to use these values, bearing in mind the fact that they are a little high, rather than to subtract fictitious values of P_A of reasonable size, which might be expected to give more nearly correct values for the moments. The good agreement of the values at different temperatures, except in the case of iodoform, indicates that they are not far from the true values. The significance of the results shown in Table IV, together with the moments of other similar molecules, will be discussed presently.

Earlier papers have discussed the variation of the polarization with concentration as evidence of the mutual effects of the polar molecules in producing orientation or association.[4] It has been shown that the orienting effect of the molecules of a liquid upon one another depends not only on the size of their electric doublets, but also upon the location of the doublet or doublets in the molecule and upon the geometrical shape of the molecule. It is interesting to compare these effects in the closely related molecules investigated in the present work.

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[3] See Smyth, THIS JOURNAL, 51, 2051 (1929).

[4] See particularly Smyth and Stoops, *ibid.*, 51, 3330 (1929); also Smyth, Chem *Reviews*, **6**, 549 (1929).

The molecule of an alkyl halide may be regarded as containing a single electric doublet located in the neighborhood of the bond between the halogen and the carbon chain. The effect of this doublet upon neighboring molecules depends upon its moment and upon the sizes of the halogen and the hydrocarbon chain which screen its force field. The deviation of the P_{12}–c_2 curves from linearity has been used as a qualitative indication of association or orientation. The effect is so great in hexane–ethyl bromide mixtures[1] that the curve actually passes through a maximum, which flattens out with rising temperature as increased thermal agitation reduces the molecular orientation. The moment of the ethyl iodide molecule is slightly smaller than that of the bromide and the screening effect[2] of the iodine is somewhat larger than that of the bromine. Consequently, the mutual effect of the molecules is not sufficient to cause a maximum in the P_{12}–c_2 curves as in the case of ethyl bromide. When butyl chloride, bromide and iodide are compared with one another, the differences are not pronounced as the screening effect of the large butyl groups so reduces the intermolecular action that the differences between the effects of the halogens are small.

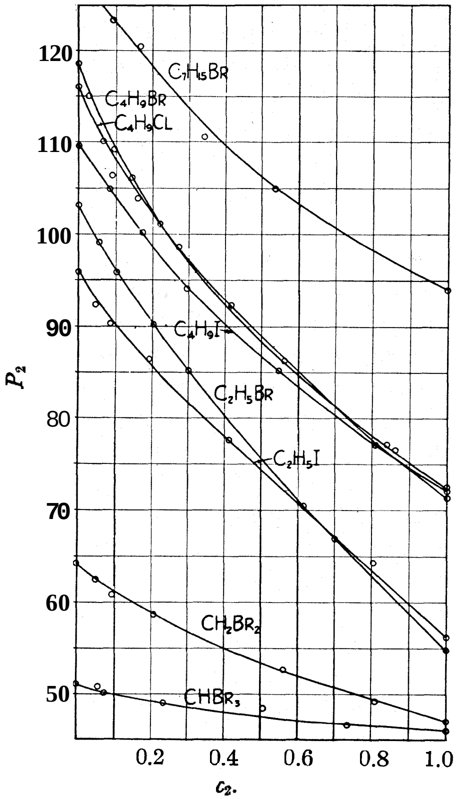

Fig. 2.—Variation of P_2 with concentration at 10°.

In comparing the P_{12}–c_2 curves for different substances, it must be borne in mind that differences in P_E affect the relative rate of change of P_2 with c_2 and hence the shape of the P_{12}–c_2 curves. Indeed, this seems to be the principal cause of the differences in these curves, for the P_2–c_2 curves in Fig. 2 show only small differences in curvature. The heptyl bromide curve has the smallest slope. The butyl halide curves have a slightly greater slope and lie close together. The ethyl bromide and ethyl iodide curves are very similar, the slope of the latter being slightly less. Differences in P_E and P_A for the different substances are responsible for the spacing of the curves.

At the bottom of the diagram lie the curves for methylene bromide and bromoform, which, because of the small size of their moments and the screening of the doublets by the bromines, show little intermolecular action. The corresponding iodine compounds are not shown, as some of their P_2 values are in error because of decomposition.

The temperature variation of P_2 for the pure substance gives further evidence of the intermolecular action. The values of P_2 for pure ethyl bromide increase slightly with rising temperature until the boiling point is approached, instead of decreasing according to the requirements of the Debye equation, because increasing thermal agitation decreases the intermolecular action which reduces the polarization. In ethyl iodide the intermolecular action is enough smaller to permit decrease of polarization with rising temperature even at the lower temperatures where its effect is greater. In the butyl halides the decrease of P_2 with rising temperature is greater and, in heptyl bromide, still greater.

The moments calculated from the values of P_∞ are given in Table IV together with a number of values previously determined, the latter being followed by their literature references.

TABLE IV

ELECTRIC MOMENTS OF HALOGEN COMPOUNDS × 10^{18}

X =	Cl	Br	I
CH_3X	1.7"	..	1.31[b]
C_2H_5X	2.0"	1.86"	1.66[d]
C_4H_9X	1.88	1.81	1.59
$C_7H_{15}X$	..	1.83	..
CH_2X_2	1.6'	1.39	1.08
CHX_3	1.05"	0.99	0.8
CX_4	0[w]	..	..
CH_3CHX_2	2.05[f]	..	..

[a] Sircar, *Indian J. Phys.*, 12, *197 (1928)*; [b] Mahanti and Sen Gupta, *ibid.*, *12, 181 (1928)*; [c] Smyth and Morgan, Ref. *1*; [d] Smyth and Stoops, **Ref.** *2*; [e] Sanger, *Physik. Z.*, 27, *556 (1926)*; [f] Ghosh, Mahanti and Sen Gupta, *Z. Physik*, *54,711 (1929)*.

The influence of the length of the carbon chain upon the moment of the molecule has been discussed previously, but a quantitative treatment of the theory has been attempted in the present investigation.[5] As the result of the treatment is not conclusive, the details are not given. The moments induced throughout the molecule by the principal doublet at the end of the chain and the moments induced in turn by these induced moments are calculated from the polarizabilities of the different parts of the molecule, which are obtained from the refractions associated with the bonds.[6] The calculated increase in moment due to the direct effect of the principal doublet is very small in the third carbon of the chain and negligible thereafter, which is in agreement with the absence of any increase in the observed

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[5] Smyth, THIS JOURNAL, *51, 2380 (1929)*.

[6] Cf. Smyth, *Phil. Mag.*, 50, *361 (1925)*.

moments with increase in the size of the alkyl group beyond ethyl. However, the secondary moments induced by those already induced by the principal doublet are calculated as continuing with decreasing size through a chain much longer than two carbons. This would cause an increase in moment with increase in the size of the alkyl group far beyond ethyl, which the agreement of the values for the ethyl and the butyl halides and, in the case of the bromides, the heptyl as well, shows to be non-existent. The rough approximations necessary in these calculations are much more apt to cause serious error in the case of the secondary moments. Indeed, they are quite sufficient to cause the not inconsiderable values calculated for these secondary moments, which the experimental results show to be negligible in the longer molecules. In view of this, it may be concluded that the results of theory and experiment are not irreconcilable, but the failure to obtain positive agreement is unsatisfactory.

The moments of the chlorinated methanes were considered at a time when very inadequate values were available.[7] It was shown that, if the tetrahedral structure of the molecule remained undistorted, the moment of methylene chloride should be 1.15 times that of methyl chloride, which should be identical with that of chloroform, while that of the symmetrical carbon tetrachloride molecule should be zero. The same relations should, of course, hold among the bromine and iodine compounds. Sänger obtained a higher value for methyl chloride than that given in Table IV, but, as Sircar's value 1.69×10^{-18} agrees well with an unpublished result obtained by Dr. S. O. Morgan, the value 1.7×10^{-18} has been adopted as correct.

The deviations of the observed values from those calculated on the basis of an undistorted tetrahedral structure may be conveniently explained by resolving the system of charges making up the methylene halide molecule into two doublets with their axes in the two imaginary lines joining the halogen nuclei to the carbon nucleus. The moment of the molecule, as a whole, is the resultant of the moments of these two doublets and is, of course, smaller the larger the angle between the axes of the doublets. The distance between a carbon nucleus and the nucleus of an attached chlorine atom is calculated to be 1.70 Å.[8] If there were no distortion of the tetrahedral structure of methylene chloride, the angle between the axes of the two doublets would be 110° and the distance between the two chlorine nuclei would, therefore, be 2.78 Å. The radius of the chlorine atom calculated by Huggins[9] from x-ray data is 0.97 Å., from which the distance between the outermost electrons in the two chlorines, a very vague quantity, would be calculated as 0.84 Å. A quantity more significant for these considerations is the atomic diameter obtained from the kinetic theory of gases, which

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[7] **Smyth,** *Phil. Mag.*, 47, 530 (1924).

[8] **Pauling,** *Z. Krist.*, 67, 377 (1928).

[9] **Huggins,** *Phys. Rev.*, 28, 1086 (1926).

might be expected to set a limit to the distance of nearest approach of the chlorine nuclei in the absence of strong forces of compression. Approximate values for this diameter may be calculated by an indirect method. The radius of the collision sphere of the argon atom determined by Rankine and Smith[10] from viscosity measurements is 1.44 Å. as compared with an atomic radius 0.93 Å. calculated by Huggins. If a proportionate difference exists for the chlorine atom, the latter has a collision sphere of radius 1.50 Å., which necessitates a distance of 3.0 Å. between the chlorine nuclei in methylene chloride if the spheres are in actual contact and uncompressed, instead of the 2.78 Å. calculated for the undistorted tetrahedral structure. A widening of the angle between the doublet axes from 110 to 124° is, therefore, required and, as a result, the moment of the molecule, as a whole, is reduced from the value calculated for the undistorted molecule, $1.15 \times 1.7 \times 10^{-18}$, to $0.94 \times 1.7 \times 10^{-18} = 1.6 \times 10^{-18}$, in agreement with the observed value. Similarly, in methylene bromide, the distance between the nuclei of the bromines and that of the carbon is given as 1.85 Å., from which the separation of the bromine nuclei may be calculated as 3.02 Å. in the absence of distortion of the tetrahedral structure. The bromine radius given by Huggins is 1.09 Å. and that of krypton is 1.06 Å., while the radius of the collision sphere of krypton found by Rankine and Smith is 1.55 Å., which figures give a radius for the sphere of repulsion of the bromine atom of 1.60 . The nuclear separation of the bromines in methylene bromide should, therefore, be 3.20 Å. instead of 3.02 Å., the angle between the doublets would be widened to 120°, and the resultant moment would be identical with that of methyl bromide. No accurate value for the latter is available in the literature, but an unpublished value determined by Dr. S. O. Morgan agrees within the limit of the experimental error with the moment of methylene bromide in Table IV. For methylene iodide, the distance between the carbon and iodine nuclei is taken as the sum of the atomic radii, 1.96 Å., and the calculation carried out as before. The angle between the doublet axes is found to be 135° and the resultant moment, therefore, 0.78 times that of methyl iodide, or $0.78 \times 1.31 \times 10^{-18} = 1.02 \times 10^{-18}$, in excellent agreement with the value in Table IV.

In similar fashion the chloroform molecule may be resolved into three doublets with their axes in the imaginary lines joining the carbon nucleus to the three chlorine nuclei which lie at the apices of an equilateral triangle. If there were no compression of the spheres of repulsion used in the calculation for methylene chloride, the carbon–chlorine bonds would be stretched even if the tetrahedral structure were so distorted that the carbon and the three chlorine nuclei were in the same plane. It appears reasonable to suppose that the hypothetical atomic spheres are somewhat compressed, but it is evident that the distortion of the tetrahedral structure of the mole-

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[10] Rankine **and** Smith, *Phil. Mag.*, **42, 601** (1921)

cule is greater than in the case of the methylene compound, which should cause the decrease in moment below that calculated for the undistorted tetrahedral structure to be greater. The separation of the chlorine nuclei is still considerably greater than the atomic diameter estimated from x-ray data, so that there is no need to suppose that the electron shells are appreciably deformed. This is in harmony with the fact that the atomic refraction of chlorine shows no significant variation between molecules containing one, two, three and four chlorines attached to the same carbon,[11] which would certainly not be the case if the electron shells of the halogens suffered increasing deformation as the number of halogens attached to one carbon increased.

Calculation leads to similar conclusions for bromoform and iodoform, although the distortion of the tetrahedral structure in the bromoform molecule should be less than in the molecules of the other two substances. Table IV shows the much lower values for the trihalogenated molecules. The moment of bromoform differs from Morgan's unpublished value for methyl bromide, to which it should be equal if the tetrahedral structure were undistorted, by an amount smaller than the differences observed for the chlorine and iodine compounds, thereby conforming with the result of the calculation. As the inductive effect of a doublet in one part of the molecule upon the rest of the molecule has been disregarded in these calculations and in view of the speculative nature of the argument concerning the atomic dimensions and the possible errors in some of the experimental values of moments quoted, the excellence of the agreement between the observed and the calculated moments of the methylene compounds must be somewhat fortuitous. It is evident, however, that the theory of the distortion of the molecule by repulsion explains satisfactorily the moments of the halogenated methanes.

Summary

The dielectric constants and densities of several alkyl halides and halogenated methanes in heptane or benzene have been determined over a wide range of temperature, and the data have been used to calculate the polarizations of the substances and the electric moments of their molecules.

The polarizations show that the orientation or association of the polar molecules depends upon the size of the electric moments of the molecules and the screening of their doublets by the molecular structure.

In the alkyl halides no measurable increase of electric moment accompanies increase of the number of carbon atoms beyond two.

In the di- and tri-halogenated methanes, repulsive forces between the halogens distort the structures and reduce the moments of the molecules.

PRINCETON, NEW JERSEY

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[11] *Cf.* Smyth, *Phil. Mag.*, **50**, **361** (1925).

[CONTRIBUTION FROM THE FRUIT PRODUCTS LABORATORY, UNIVERSITY OF CALIFORNIA]

THE EFFECT OF SEVERAL FACTORS ON THE SOLUBILITY OF TARTRATES

BY P. H. RICHERT

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During investigations on the removal of tartrates from certain grape products, it became necessary to determine the solubility of tartrates under certain conditions. Potassium bi-tartrate and neutral calcium tartrate were the salts particularly concerned.

A review of the literature indicates that considerable data already exist on tartrate solubilities, although much of the data desired in our studies could not be found in published form.

The change of solubility with temperature has been determined for the range from 0 to 100°[1] for both salts. Solubilities in the presence of certain ions and in certain acids have been determined to some extent. The published data indicate that ions common to the salt concerned usually depress the solubility, and that neutral ions have little effect on the solubility.

No information could be found on the effect of neutral potassium tartrate on the solubility of potassium bi-tartrate. In this case the added salt has two ions in common with the salt studied. It would be expected that the solubility of the potassium bi-tartrate would be decreased to an appreciable extent by the presence of neutral potassium tartrate. The results tabulated below and shown in Fig. 1 indicate this to be the case to a very marked degree, especially at the lower concentrations of the neutral tartrate.

TABLE I

SOLUBILITY OF $KHC_4H_4O_6$ IN THE PRESENCE OF $K_2C_4H_4O_6$ AT 20°

Mole of $KHC_4H_4O_6$/liter	Mole of $K_2C_4H_4O_6$/liter	Mole of $KHC_4H_4O_6$/liter	Mole of $K_2C_4H_4O_6$/liter
0.0284	0	0.00667	0.00443
.0218	0.000443	.00540	.00714
.0176	.000886	.00360	.0143
.0124	.00177	.00280	.0214
.0096	.00266	.00264	.0286
.00805	.00354	.00260	.0357

The fact that very small concentrations of neutral tartrate greatly affect the solubility of the bi-tartrate may explain the formation of large deposits of cream of tartar in juice from mature grapes, and in grape juice after standing for some time, since under these conditions the acidity is decreased, forming the neutral tartrate which depresses the solubility of the remaining bi-tartrate.

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[1] Seidell, "Solubilities of Inorganic and Organic Compounds," Vol. I, pp. 221, 564.

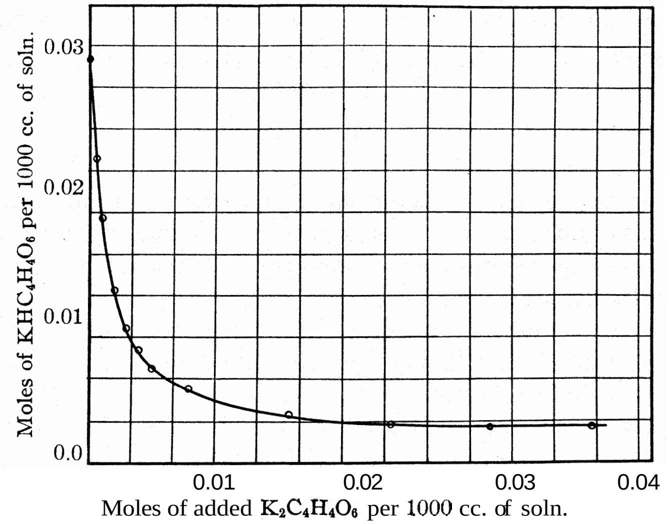

Fig. 1.—The effect of $K_2C_4H_4O_6$ on the solubility of $KHC_4H_4O_6$ in water at 20°.

Tartaric acid was found to have some effect on the solubility of potassium bi-tartrate in concentrations up to about 0.01 mole per liter. This is shown in Table II and Pig. 2.

TABLE II

SOLUBILITY OF $KHC_4H_4O_6$ IN TARTARIC ACID SOLUTIONS AT 20°

Mole of $KHC_4H_4O_6$/liter	Mole of $H_2C_4H_4O_6$/liter
0.0284	0
.0268	0.0030
.0260	.0055
.0240	.0105
.0238	.0335
.0238	.0485

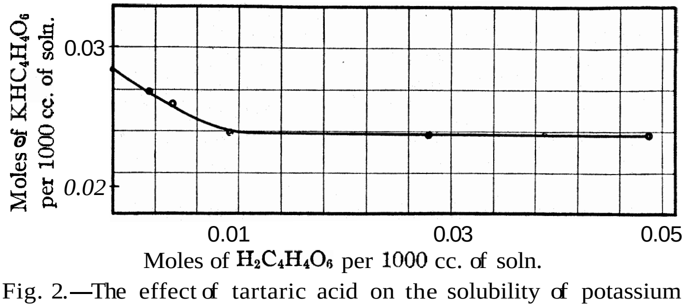

Fig. 2.—The effect of tartaric acid on the solubility of potassium bi-tartrate in water at 20°.

From the data of Table II considered in comparison with Table I, it would seem that the effect of tartaric acid is due chiefly to the ions produced, rather than to the tartaric acid molecule itself.

The solubility of potassium bi-tartrate was also determined in invert sugar solutions. The results appear in Table III and in the solid curve of Fig. 3.

TABLE III

SOLUBILITY OF $KHC_4H_4O_6$ IN INVERT SUGAR SOLUTIONS AT 20°

Soly. of $KHC_4H_4O_6$ in mole per liter	Soly. of $KHC_4H_4O_6$ in mole per 1000 g. soln.	Percentage invert sugar by weight
0.0284	0.0284	0
.0276	.0260	15
.0264	.0232	30
.0240	.0198	45
.020	.0155	60
.0124	.0087	80

TABLE IV

SOLUBILITY OF CALCIUM TARTRATE IN TARTARIC ACID SOLUTIONS

Mole of $H_2C_4H_4O_6$ per liter	Mole of $CaC_4H_4O_6$ per liter at 20°	Mole of $CaC_4H_4O_6$ per liter at 18° (Paul, 1915)[a]
0	0.00253	0.00244
0.0067	0.00399	.00350
.0134	....	.00445
.0268	.00677	.00581
.0402	....	.00678
.0469	.00810	....
.0536	....	.00758
.0670	.00910	.00848

[a] Ref. 1, pp. 221, 222.

The dotted line in the curve indicates the theoretical solubility curve, if the solvent action were due solely to the water present. Thus it can be seen that the presence of the sugar has a slight solvent action on the potassium bi-tartrate.

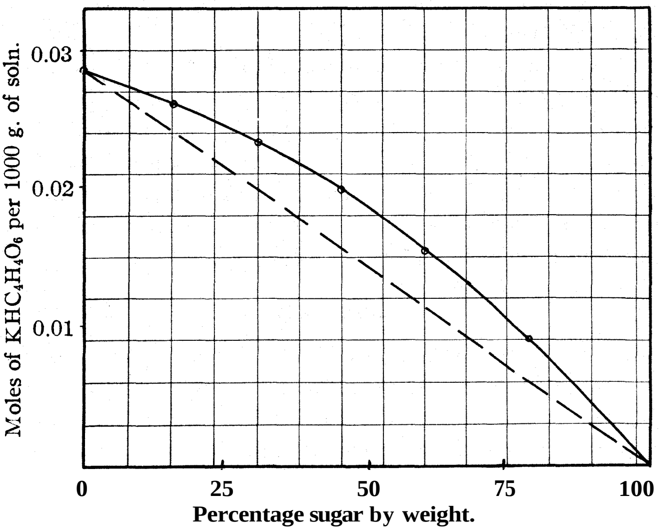

Fig. 3.—The solubility of potassium bi-tartrate in invert sugar solutions at 20°.

For calcium tartrate the solubility in hydrochloric and tartaric acids[2] has been determined for 18°. The solubility in tartaric acid solutions was

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[2] Ref. 1, pp. 221, 222.

determined for 20° and the results are given in Table IV and in Fig. 4. The two curves seem to agree quite well.

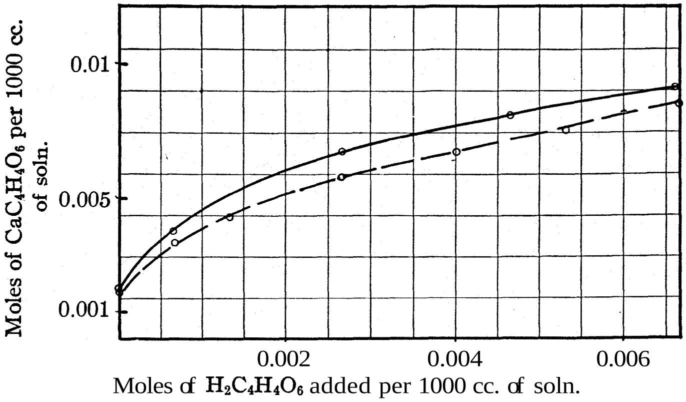

Fig. 4.—The solubility of calcium tartrate in dilute tartaric acid solutions: solid line is solubility at 20"; dotted line is solubility at 18° (Ref. a, Table IV).

Method of Analysis.—In all cases the salt of which the solubility was to be determined was added to the solution in excess. The mixture was stirred for at least an hour with a mechanical stirrer, and allowed to settle for several hours at 20° before filtering and analyzing. No precaution was taken to exclude the presence of carbon dioxide from the air, but since the solutions were all acid it was believed that carbon dioxide would have little effect. All of the data for the potassium bi-tartrate were obtained by titration with $N/10$ sodium hydroxide. For the calcium tartrate solubilities, ash determinations were made on the solutions.

Summary

The solubilities of potassium bi-tartrate in the presence of some of the substances with which it is associated in grape juice were determined. Some of these, especially the neutral tartrate, have a rather striking effect on the solubility of the bi-tartrate and this fact may help to explain the rather peculiar behavior of cream of tartar in grape juice.

Some solubility data on calcium tartrate were obtained which seem to agree well with previously published data.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ELECTRICAL CONDUCTANCE OF AQUEOUS SOLUTIONS OF BARIUM CHLORIDE AS A FUNCTION OF THE CONCENTRATION

BY GRINNELL JONES AND MALCOLM DOLE

RECEIVED DECEMBER 31, 1929 PUBLISHED JUNE 6, 1930

Introduction

This is the third of a series of papers on the properties of solutions of barium chloride and is part of an extensive experimental investigation of the properties of these solutions covering a wide range of concentration which was undertaken in the hope that the data when studied in the light of the new Debye–Hückel theory of electrolytes would reveal new laws for the variation of these properties with the concentration or new relationships between the properties. Barium chloride is well adapted for this purpose because the theory and the known facts indicate that the influence of interionic attraction increases greatly with the valence. The first paper[1] in this series records data on the transference numbers of the barium ion covering the range 0.01 to 1.0 molal which resulted in the discovery of a new law for the variation of the transference numbers with the concentration. The second paper[2] contains new data on the viscosity of these solutions covering the range 0.005 to 1.0 molal and a new general law for the variation of the viscosity of solutions of electrolytes with the concentration. In this paper are recorded data on the conductance of this salt covering the range 0.001 to 1.0 molal which have suggested an equation for the variation of the conductance with concentration. All of these properties of these solutions turn out to be functions of the square root of the concentration.

Experimental Part

The barium chloride was purified as already described.[3] To prepare neutral solutions of known composition the salt was dried by heating to a low red heat in a current of hydrochloric acid in a Richards[4] bottling apparatus, and cooled in a vacuum. The solutions were made by weight, using conductivity water of known conductance. After the salt had dissolved and had been well mixed by shaking, a portion was withdrawn to test its neutrality. It was found that methyl red when added to solutions of barium chloride was sensitive to a trace either of hydrochloric acid or of barium hydroxide. Therefore, methyl red was added to the sample of the solution prepared as described above and also to a solution of approximately the

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[1] Grinnell Jones and Malcolm Dole, THIS JOURNAL, 51, 1073 (1929).

[2] Grinnell Jones and Malcolm Dole, *ibid.*, 51, 2950 (1929).

[3] Grinnell Jones and Malcolm Dole, *ibid.*, 51, 1074 (1929).

[4] T. W. Richards and H. G. Parker, *Proc. Am. Acad.*, 32, 59 (1896).

same composition prepared from crystallized unheated barium chloride and the solution was rejected if the two could be distinguished. After the proper technique of drying the salt had been developed the solutions always gave the same color.

The stopper was then replaced by a special ground-glass stopper provided with two tubes, one of which extended to the bottom of the bottle and was connected by a ground joint with the conductivity cell. Air which had been bubbled through a barium chloride solution of approximately the same concentration was then blown into the bottle through the other tube. thus forcing the solution into and through the conductivity cell until the cell was well rinsed without danger of changing the composition of the solution by evaporation. The cell was then tightly closed by its own glass stoppers and placed in the thermostat at 25.00° and its resistance measured. It was then refilled and measured again. Only rarely was any change noted and in such cases the rinsing was repeated until successive fillings gave concordant results. The density of the solution was then determined by an Ostwald pycnometer to permit calculation of the concentration in moles per liter. The resistance measurements were made by the special bridge already described by Jones and Josephs[5] using all precautions recommended in that paper. The results with 1100 cycles and with 2500 cycles agreed within 0.01%.

All solutions more dilute than 0.01 molal were prepared by dilution by weight of a 0.01 molal solution.

Three different cells of the Washburn pipet type with cell constants of 144.65, 51.4953 and 1.2326 were used. The cell constants of the first two were determined by means of a 0.01 N solution of potassium chloride in accordance with the suggestion of Kraus and Parker? The cell constant of the third cell was found by intercomparison with the second. The standard reference solution had 7.4945 g. of potassium chloride dissolved in 1000.00 g. of water (both weighed in air uncorrected to vacuum). The specific conductance of this solution was taken to be 0.0128988 plus the specific conductance of the water used. This value corrects for a slight inconsistency in Kohlrausch's figures for the N KC1 and the 0.1 N KC1 standards of reference but it is based on Kohlrausch's absolute measurements.

We are aware that H. C. Parker and E. W. Parker[7] have concluded as the result of a careful investigation that the absolute measurements of the specific conductance of the standardizing solutions by Kohlrausch are in error by more than 0.1%. Parker and Parker have utilized fully the best of the earlier technique and have made important improvements in the details of procedure and valuable suggestions as to definitions of units,

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[5] Grinnell Jones and R. C. Josephs, THIS JOURNAL, 50, 1049 (1928).

[6] C. A. Kraus and H. C. Parker, *ibid.*, 44, 2422 (1922).

[7] H. C Parker and E. W. Parker, *ibid.*, 46, 312 (1924)

but their bridge assembly has since been shown to be imperfect,[8] and the pipet cells of the type used show an apparent variation of cell constant with the resistance of the solution being measured, which was discovered by H. C. Parker[9] and Randall and Scott.[10] This Parker effect is ascribed by him to absorption at the electrodes and walls but he did not succeed in finding a practical means of avoiding the effect. Parker and Parker believe that this effect was present in the cells used in their absolute measurements (Ref. 7, p. 324), and although they attempt to minimize this error by the device of subtracting the measured resistance of two cells, they show a commendable lack of enthusiasm for this procedure, which is based on the unproved (and in our judgment unprovable) assumption that the electrode effects cause an equal error in the resistance of two cells of different cell constant and design. It therefore seemed to us premature to adopt the figures of Parker and Parker for the specific resistance of solutions of potassium chloride as a basis for determining the cell constant unless and until their results are confirmed by an independent investigation. Our opinion in this matter is not altered by the fact that the figures of Parker and Parker are used as the basis for conductance data in Vol. VI of the "International Critical Tables," which has been published during the final stages of the preparation of the manuscript of this paper.

It is believed that uncertainty of greater than 0.02% in the data on barium chloride solutions due to the Parker effect[g] was avoided by always selecting a cell which would give a resistance of above 1000 ohms and by the use of the Jones and Joseph's bridge.[11]

The data are recorded in Table I, in which each horizontal row represents a different solution and in which the columns give in order (1) the concentration in gram molecules ($BaCl_2$) per liter, *c*, based on weights in *vacuo* (the molecular weight of barium chloride being taken as 208.284); (2) the square root of the concentration, $\sqrt{c}$; (3) the density, d, absolute with vacuum corrections applied; (4) density computed from the formula given below; (5) the difference between the observed and computed density; (6) the measured molecular conductance, Λ obs.; (7) a correction to give the conductance at the nearest round concentration, $\Delta\Lambda$; (8) the corrected values at the round concentration indicated, Λr. The density

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[8] Compare Parker and Parker, Ref. 7, p. 314, with Jones and Josephs, THIS JOURNAL, 50, 1058–1062, 1070–1074 (1928).

[9] H. C. Parker, *ibid.*, 45, 1366, 2019 (1923).

[10] M. Randall and G. N. Scott, *ibid.*, 49, 636 (1927).

[11] The question of the cause and cure for the Parker effect has been investigated further in this Laboratory since the experimental work described in this paper was completed. This later work has disclosed that although the cells used in the research described in this paper embodied all principles of good design known at the time, they are not as free from Parker effect as some cells built in this Laboratory subsequently. A paper on cell design including a discussion of the Parker effect is now in preparation.

data when treated by the method of least squares gave $d = 0.99707 + 0.18224c - 0.00421c^2$. The maximum deviation between the observed results and computed results is 0.00006 and the average deviation is 0.00003.

TABLE I

MOLECULAR CONDUCTANCE OF BARIUM CHLORIDE SOLUTIONS AT 25°

Gram moles per liter	$\sqrt{c}$	Density, d, obs.	Density computed	Difference	A obs., conductance	ΔΛ Correctton to round concn.	Λr Conductance at round concn.
0.0009827	0.031348	.....	0.99725	....	264.70	−0.13	264.57
.0009701	.031146	.....	.99725	....	264.72	−0.23	264.49
						Mean A at *c* = 0.001	264.53
.0024547	.049545	.....	.99752	....	256.46	−0.19	256.27
.0024969	.049969	.....	.99753	....	256.25	−0.01	256.24
						Mean A at *c* = 0.0025	256.25
.0049940	.070668	0.99801	,99798	\$0.00003	248.14	−0.02	248.12
.0051560	.071805	.....	(.99801)	....	247.70	+0.40	248.10
						Mean A at c = 0.005	248.11
.009999	,099995	0.99890	.99889	+ .00001	238.273	−0.001	238.27
.009999	.099995	.....	(.99889)	....	238.274	−0.001	238.27
						Mean A **at** *c* = 0.01	238.27
.025002	.15812	1.00163	1.00163	....	223.25	−0.00	223.25
.025000	.15811	.....	(1.00163)	....	223.24	0.00	223.24
						Mean A at *c* = 0.025	223.25
.049986	.22358	.....		....	210.656	−0.005	210.65
.049998	.22360	1.00621	1.00617	+ .00004	210.652	−0.001	210.65
						Mean A **at** *c* = 0.05	210.65
.100009	.31624	1.01531	1.01525	+ .00006	197.358	+0.002	197.36
.099995	.31623	.....	(1.01525)	....	197.370	−0.001	197.37
						Mean A at *c* = 0.10	197.36
.250044	,50004	1.04240	1.04238	+ .00002	178.388	+0.004	178.392
.249992	.49999	1.04236	1.04237	− .00001	178.398	−0.001	178.397
						Mean A **at** *c* = 0.25	178.39
.50000	.70715	1.08711	1.08714	− .00003	161.184	+0.000	161.184
.50000		1.08708	1.08714	− .00006	161.226		161.22_6
						Mean A at c = 0.50	161.20
.97476	,98730	1.17066	1.17071	+ .00005	138.982	−1.039	137.94
1.00527	1.00263	1.17601	1.17602	− .00001	137.764	+0.217	137.98
						Mean Λ at *c* = 1.0	137.96

The uncorrected data shown in Col. 6 are represented in Fig. 1 by the center points of the circles. In most cases the two independent determinations on solutions of nearly the same concentration are shown by a single circle because the slight differences are not visible on the scale which can be printed.

The corrections to bring the values to round concentrations were determined by plotting A against $\sqrt{c}$, the slope of the curve $d\Lambda/d\sqrt{c}$ was found at each point and the correction $M = (d\Lambda/d\sqrt{c})\Delta\sqrt{c}$ computed and applied. It will be noticed that after correction to a common round concentration each pair of solutions of similar concentration agree very well, the average deviation being only 0.025 ohm. These differences are greater in the most dilute solutions, as is to be expected on account of the greater experimental difficulties in working with dilute solutions.

Interpretation of the Data

Having obtained a set of data covering a wide range of concentration it becomes of interest to attempt to find an equation for the molar conductance as a function of the concentration which is in harmony with the data and of a form which is as simple as possible and which shows no abnormal or improbable behavior as the concentration approaches zero; and to use the best equation which can be found to estimate the limiting conductance at zero concentration. It seemed hardly necessary to carry out the laborious calculations with all of the numerous equations which have been proposed because nearly all of the empirical equations which antedate the Debye-Hückel theory are now known to be inaccurate or to be in harmony with the facts only within a quite limited range of concentration.

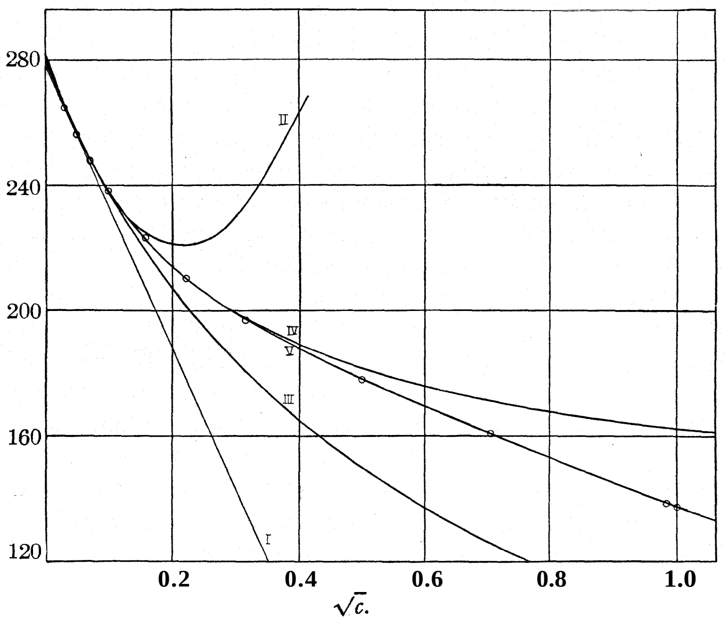

Fig. 1.—I, Kohlrausch, A = $278.75 - 449.9\sqrt{c}$; II, Debye–Hückel–Onsager, A = $280.64 - 550.12\sqrt{c} + 1265.1c$; III, Walden, A = $278.69/(1 + 1.715\sqrt{c})$; IV, Lattey, A = $281.22 - [602.8\sqrt{c}/(1 + 4.069\sqrt{c})]$; V, Jones and Dole, A = $282.13 - [636.3\sqrt{c}/(1 + 4\ 628\sqrt{c})] - 31.13\,c$.

Recently Debye and Hückel[12] have proposed a theory of electrolytes based on the hypothesis that ionization is substantially complete and that the electric forces between the ions which Arrhenius assumed to be negligible play a significant role.

The mathematical complexities of deriving definite equations on this

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[12] P. Debye and E. Hückel, *Physik. Z.*, 24, 185 (1923); 24,305 (1923); E. Hückel, *Ergebnisse der Exakten Wissenschaften*, 3, 199 (1924).

basis are very great and compel them to neglect some known physical factors in the problem and to introduce some relatively simple approximate mathematical relationships instead of using the rigid but more complicated functions. Their conclusion is that the equation

$$\Lambda = \Lambda_0 - A\sqrt{c} \tag{I}$$

is the limiting law to which the measured conductance will approach more and more closely as the concentration approaches zero. The constant A has a very complicated theoretical significance, being dependent upon the dielectric constant of the solvent, the temperature, the mobilities at infinite dilution and valence of all of the ions present, as well as several universal constants. However, the value of A as well as Λ_0 is in practice chosen to fit the data. It should be noted, however, that the theory predicts that the most important factor in determining the variation of A from salt to salt is the valence type and this prediction is borne out in practice. Indeed it has long been known that the conductance–concentration curves of all salts of the same valence types (in the absence of abnormalities such as complex formation) tend to run parallel and near together, whereas the curves for salts of different types diverge markedly.

This Equation I was discovered long ago by Kohlrausch,[13] was much used by him in extrapolating to zero concentration and is commonly called Kohlrausch's square root law. The most convenient way to test the validity of this law is to plot the observed values of the conductance against the square root of the concentration and observe how closely the points fall on a straight line. A straight line (I in Fig. 1) having the equation $\mathbf{A} = 278.75 - 449.9\sqrt{c}$, passes through the values of A at 0.001 and 0.0025, but this line deviates greatly from the data at all higher concentrations. Kohlrausch's law can, therefore, only be regarded as a limiting law which is approximately obeyed in very dilute solutions. This is evident from Col. 5 of Table II and from Fig. 1, in which our data are plotted as points within the circles and Curve I represents the equation given above. Space does not permit a detailed recapitulation and analysis of the evidence from other cases in the literature but much can be found. The case of barium chloride cited from our own data is typical rather than exceptional or peculiar.

But although Kohlrausch's law can only be regarded as a limiting law, the experimental evidence in its favor and the theoretical support which it receives from the work of Debye and Hiickel make it extremely probable that the true equation expressing the conductance as a function of the concentration when plotted A against $\sqrt{c}$ will be asymptotic at $c = 0$ with a straight line having finite negative slope. In attempting to find an

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[13] F. Kohlrausch and M. E. Maltby, *Wiss. Abh. Phys. Techn. Reichanstalt*, **3**, 156–227 (1900); F. Kohlrausch and E. Grüneisen, *Berl. Ber.*, 1215–1222 (1904); F. Kohlrausch, *Z. Elektrochem.*, 13, 336 (1907); 13, 645 (1907); F. Kohlrausch, "Gesammelte Abhandlungen," 1911, Vol. II, pp. 901, 1083, 1127, 1148.

equation which is valid up to as high a concentration as possible, we have applied this criterion and rejected all forms of the function which do not meet this test.

TABLE II

CALCULATED AND OBSERVED VALUES

Concn. c	$\sqrt{c}$	A Obs. conductance	I Kohlrausch $A = 27875 - 449\ 9\sqrt{c}$ A comp.	ΔΛ	II Debye–Hückel $A = 280.64 - 550\ 12\sqrt{c} + 1265.1c$ A comp.	ΔΛ
0 001	0.031623	264.53	264.53	$000	26451	+0.02
.0025	05	256 25	256.25	+0.00	256.30	−0 05
.005	.070711	248.11	246.94	+1.17	248.07	+0 04
01	.1000	238 27	233.76	. +4 51	238 28	−0 01
025	15811	223.25	207.61	$15.64	225.29	−2 04
.05	22361	21065	178.15	+32.50	22089	−10 24
.1	.31623	197.36	136.48	+60 88	233.19	− 35 83
.25	.50000	178 39	53 80	$124 59	321 86	−143 46
50	.70711	161 20	−39 38	+200 58		
1 00	1 00000	137.96	−171 15	+309 11		

Concn	$\sqrt{c}$	Obs conductance	III Waiden $\Lambda = \frac{278\ 69}{1 + 1.715\sqrt{c}}$ A comp.	ΔΛ	IV Lattey $\Lambda = 281.22 - \frac{[illegible]}{1+4.069\sqrt{c}}$ A comp.	ΔΛ	V Jones and Dole $\Lambda = 282\ 13 - \frac{[illegible]}{1+4.628\sqrt{c}} - 31.13c$ A comp.	ΔΛ
0 001	0.031623	264 53	264 *25*	+0.28	264 33	+0.20	264 55	−0 02
.0025	.05	256 25	256.65	−0.44	256 16	+0 09	256.22	+ .03
.005	,070711	248 11	248.56	−0.45	248 10	+0 01	248 03	+ .03
.O1	.1000	238.27	237.89	+0 38	238 37	−0.10	238 32	− .05
.025	15811	223 25	219 24	+4 01	223.22	+0 03	223 26	− .O1
.05	.22361	210 65	201.44	+9 21	210 64	+0 01	210 65	+ 00
.1	31623	197 36	180.69	+16 67	197 86	−0 50	197 36	+ .02
.25	,50000	178 39	150.04	+28 35	181 90	−3 51	178 *35*	+ 04
.50	.70711	161 20	125 95	+35 25	171 28	−10 08	161 26	− .06
1.00	1 00000	137 96	100 03	+37 93	162 30	−24 34	137.94	+ .02

The next form of the conductance function to be considered was a modification of Kohlrausch's law having the form

$$A = \Lambda_0 - A\sqrt{c} + Bc \qquad \text{(II)}$$

This equation obviously meets the asymptotic test given above. It was first suggested by Debye and Hiickel in their early paper and used as a means of extrapolating to infinite dilution, but since the last term has no theoretical basis it may be regarded as an empirical equation. Debye and Hiickel chose values of Λ_0, A and B empirically to fit the data. Onsager[14] points out that the space lattice arrangement postulated by Debye and Hiickel must be disturbed by Brownian movement and has worked out a mathematical technique to make allowance for this disturbance and to take account of the combined relaxation of the ionic atmospheres due to the

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[14] L. **Onsager**, *Physik. Z.*, *27*, **388** (1926); 28, 277 (1927); *Trans. Faraday Soc.*, 23, 341 (1927).

diffusion of the ions in respect to one another and to enable the effect of electrophoresis to be calculated without a knowledge of ionic radii. Onsager's derivation leads to an equation of the form of Kohlrausch's square root law in which the slope A is a complicated but explicit function of the dielectric constant and viscosity of the solvent, the temperature and the valencies and mobilities at infinite dilution of all of the ions present, as well as several universal constants. Ionic radii are, however, not involved directly. Assuming the conductance of the ions at infinite dilution to be known, Onsager has computed the slope of the Λ–$\sqrt{c}$ curves for many salts with results which agree within about 10% with the slopes found experimentally; but although this does not solve the problem of extrapolation to infinite dilution, because for this purpose we need to know the slope with an uncertainty of much less than 10% in order to find the limit of the conductance at infinite dilution, nevertheless it is of much interest.

Onsager recognizes that an equation of the form of Kohlrausch's law which he has derived is only valid as a limiting law and in order to extend its range of validity he follows Debye and Hückel in adding a term, $+Bc$, linear with the concentration. The equation

$$\Lambda = \Lambda_0 - A\sqrt{c} + Bc \qquad \text{(II)}$$

is an improvement over the Kohlrausch equation but no claim is made by its proponents that it is valid above 0.01 molal. We have found that an equation of this form

$$\Lambda = 280.64 - 550.12\sqrt{c} + 1265.1c$$

fits our data on barium chloride fairly well up to 0.01 molal (see Curve II in Fig. 1 and Cols. 6 and 7 in Table II) but it fails badly in higher concentrations. This is the equation of a parabola (when plotted Λ against $\sqrt{c}$) with a minimum value of Λ at $\sqrt{c} = 0.217$ or $c = 0.048$, whereas the data show no indication of the occurrence of a minimum. Beyond this minimum this equation gives grossly erroneous results. It is quite evident from the curves and computations that the term $+Bc$ is at fault.

The complicated and difficult derivations of this equation evidently and admittedly fail to account adequately and fully for all of the factors in the problem. In these circumstances we thought it best to attempt to find a valid equation by inductive methods from the data themselves rather than by deductive reasoning from hypotheses.

Walden[15] has proposed an equation of the form

$$\Lambda = \frac{\Lambda_0}{1 + N\sqrt{c}} \qquad \text{(III)}$$

and has presented considerable evidence in its support, especially for non-aqueous solutions. It is easy to show by differentiation that this equation conforms to the asymptotic test described above. The Walden equation

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[15] P. Walden, *Z. physik. Chem.*, 108, 341 (1924).

can be readily transformed into $1/\Lambda = 1/\Lambda_0 + N/\Lambda_0\sqrt{c}$, which permits its validity to be tested by plotting $1/\Lambda$ against $\sqrt{c}$, and the coefficients to be readily determined. We used our data on barium chloride at c = 0.01 and below to evaluate the constants and thus obtained $A = 278.69/(1 + 1.715\sqrt{c})$. This equation comes much nearer to the experimental values at the higher concentrations than either of the forms already discussed but, nevertheless, it is not within the experimental errors either at low or high concentrations and indeed is not as good at low concentrations as Equation I or II (see Curve III in Pig. 1 and Cols. 8 and 9 in Table II).

Lattey[16] has recently suggested the form

$$\Lambda_0 - \Lambda = \frac{A}{V^{1/2} + N}$$

where $V = 1/c$ and A and N are dependent on the salt chosen and the temperature. This may be readily transformed into

$$\Lambda = \Lambda_0 - \frac{A\sqrt{c}}{1 + N\sqrt{c}} \qquad \text{(IV)}$$

Lattey in a brief paper gives calculations showing that an equation of this form, $\Lambda = 130.01 - [89.47\sqrt{c}/(1 + 1.82\sqrt{c})]$, agrees with the data of Kohlrausch and Maltby on potassium chloride up to 1 molal. He states that he has tested it on many other univalent salts and finds that it conforms to the facts up to 0.1 molal, but does not publish the proof in detail. His paper contains no indication that he has tested his equation on salts of higher valence types. This equation is obviously asymptotic to $\mathbf{A} = \Lambda_0 - A\sqrt{c}$ as $\sqrt{c}$ approaches zero. We then applied the method of least squares to the data on barium chloride up to 0.05 to determine the best values of the coefficients with the result $A = 281.22 - [602.8\sqrt{c}/(1 + 4.069\sqrt{c})]$. As will be seen from Cols. 10 and 11 of Table II and Curve IV in Fig. 1, this equation is a very substantial improvement over the other forms already discussed. The Lattey equation agrees with the data within the experimental error up to 0.05 molal, but if the constants are chosen so as to give good agreement at these concentrations the computed values of A at the higher concentrations are too great.

We noticed that these deviations of the Lattey equation seemed to be proportional to the concentration and this suggested to us that they might be remedied by adding a term, $-Bc$ giving an equation of the form

$$\Lambda = \Lambda_0 - \frac{A\sqrt{c}}{1 + N\sqrt{c}} - Bc \qquad \text{(V)}$$

The constants of this equation were determined by the method of least sauares to be

$$\Lambda = 282.13 - \frac{636.3\sqrt{c}}{1 + 4.628\sqrt{c}} - 31.13c, \text{ or}$$

$$\frac{\Lambda}{282.13} = 1 - \frac{2.1845\sqrt{c}}{1 + 4.628\sqrt{c}} - 0.1103c$$

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[16] **R.** T. Lattey, ***Phil.*** Mag., [7] 4, 831 (1927).

This equation fits the data within 0.06 mho at all points from 0.001 to 1.0 molal. The average deviation is only 0.014%. Curve V in Fig. 1 is the graph of this equation and the experimental points are the centers of the circles. The deviations are much too small to be apparent in the graph on the scale which can be printed but are shown numerically in the last column of Table II.

A discussion of the general validity of Equation V will be postponed until new data on many salts covering a wide range of concentration can be obtained. In view of the fact that important improvements in the design of cells for the measurement of conductance have recently been effected in this Laboratory, it seems inadvisable to undertake the laborious calculations necessary to test this equation by means of the data existing in the literature. The correlation of these conductance data with our transference data will be discussed in a separate paper by the junior author.

The Viscosity Correction

In the above theoretical treatment no attempt has been made to apply to the conductance data a viscosity correction.[17] During the course of the experimental work, measurements were made to determine the viscosity of barium chloride solutions. These results have already been published.[2] Although these data were originally obtained in the expectation of using them to correct the conductance values for the viscosity changes, a careful consideration of the question suggests that a large part if not all of the viscosity correction should not be applied. By studying our viscosity data we discovered that the relative fluidity (φ) of the solution could be expressed accurately by an equation of the form

$$\varphi = 1 - A\sqrt{c} - B(c) \qquad \text{(VI)}$$

or for viscosities in dilute solutions

$$\eta = 1 + A\sqrt{c} + (B + A^2)(c) + \ldots \qquad \text{(VII)}$$

A and B are constants chosen to fit the data. For barium chloride solutions at 25°, $A = 0.02013$ and $B = 0.20087$. The square root term suggested to us that this part of the viscosity increase might be due to the electric forces existing between the ions.

Falkenhagen and Dole[18] have deduced from the Debye theory of interionic attraction that the distortion of the symmetrical ionic arrangement by means of viscous flow increases the macroscopic viscosity of the solution in proportion to the square root of the concentration; but the friction encountered by an ion moving in an electric field is determined by the microscopic viscosity of the water molecules in its immediate path and this microscopic viscosity is probably not identical with the macroscopic viscosity as determined in a viscometer.

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[17] *See* C. A. Kraus, THIS JOURNAL, *36*, 35 (1914), for a historical review of this question.

[18] H. Falkenhagen and M. Dole, *Physik. Z.*, 30, 611 (1929).

If the electric forces between the ions really change the microscopic viscosity, then this would influence the motion of the ions and would need to be taken into account in considering the variation of conductance with concentration. In such a case it would be fallacious to use Stokes' law without allowing for the change in viscosity. But if the microscopic viscosity is unaffected by the interionic attraction, it would be erroneous to apply a viscosity correction to the data for the change in macroscopic viscosity due to the interionic attraction represented in our viscosity equation (VII) by the term $A\sqrt{c}$.

This may also be true for the Bc term of Equation VI. Thus MacInnes and Cowperthwaite[19] have found that the conductance of the chloride ion is exactly the same in 0.1 normal solutions of sodium chloride and of potassium chloride although the measured macroscopic viscosities differ by 2%. This identity of the mobility of the chloride ion in the two solutions indicates that the effective or microscopic viscosity of the medium in the path of the moving ion may be the same in the two solutions.

This evidence against applying any viscosity correction is not entirely unambiguous since the junior author has discovered in some unpublished work that ions apparently affect macroscopic viscosities quite independently of each other, at least as regards the B terms of Equation VI. If this is true, then it is possible for the chloride ion to migrate in an environment whose microscopic viscosity is determined only by the chloride on itself. and thus have the same conductance either in sodium or potassium cihloride However, new experiments must be carried out before this question can be entirely settled.

Grateful acknowledgment is made for an appropriation from the Milton Fund of Harvard University for the expenses of this work.

Summary

1. Measurements of the density and electrical conductance of aqueous solutions of barium chloride at 25° covering the range 0.001 to 1.0 molal are recorded.

2. Numerous functions which have been suggested to express the variation of the conductance with the concentration are discussed and a new function having the form, $\Lambda = \Lambda_0 - [A\sqrt{c}/(1 + N\sqrt{c})] - Bc$ is shown to be in harmony with the facts in this case, over the range 0.001 to 1.0 molal.

3. The propriety of applying a viscosity correction to measurements of conductance is discussed.

4. In this and the preceding papers of this series it is shown that the properties of aqueous solutions of barium chloride at 25° can be expressed as a function of the concentration up to 1 molal by the equations

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[19] D. A. MacInnes and I. A. Cowperthwaite, *Trans. Faraday Soc.*, **23,** 400 (1927).

Activity coefficient $\log f = \frac{-1.734\sqrt{c}}{1 + 2.2318\sqrt{c}} + 0.15266c$

Transference number of the barium ion $t = \frac{1.4476}{1 + 0.07010\sqrt{c}} - 1$

Relative fluidity $\varphi = 1 - 0.02013\sqrt{c} - 0.20087c$

Density $d = 0.99707 + 0.18224c - 0.00421c^2$

Molal conductance $A = 282.13 - \frac{636.3\sqrt{c}}{1 + 4.628\sqrt{c}} - 31.13c$

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THE OXYGEN ELECTRODE: AN ADSORPTION POTENTIAL

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The problem of the oxygen electrode arose, for the most part, from the study of the Grove cell: Pt, HNO_3, H_2SO_4, Zn. This cell gives, when freshly made, a potential of 1.6 to 1.7 volts. It is extremely sensitive to polarization effects, which change the potential over a considerable range and render it irreproducible. The cause of this polarization was supposed to be some reaction involving the transfer of oxygen from the gaseous to an ionic or combined state. The outcome was that the study of the oxygen electrode was approached from the standpoint of polarization reactions.

One very prevalent explanation of the behavior of this electrode is the formation of various oxides of platinum and their hydrates; the so-called "oxide theory."[1] Another theory is that the potentials are due to the formation of unstable products in the electrolyte about the electrode.[2] The experimental work described in the literature just cited affords abundant evidence that the oxygen electrode is irreversible, and cannot be classed with the hydrogen electrode or metal electrodes against solutions of their ions. As a matter of fact, there is no experimental evidence to show that there is any chemical reaction at the electrodes.

Recently, efforts based upon purely empirical considerations have been made to use the oxygen electrode in electrometric titrations involving oxidizing solutions.[3]

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[1] G. Grube, *Z. Elektrochem.*, 16, *621–632 (1910);* R. Lorenz and co-workers *ibid.*, 15, *206–212, 293–297,* 349–355 *(1909);* F. Foerster, *Z. physik. Chem.*, *69,* 236–*271 (1910);* Spielman, *Trans. Faraday Soc.*, *5,* 88–102 *(1909);* G. Grube and B. Dulk, *Z. Elektrochem.*, 24, *237–248 (1918);* E. P. Schoch, *J. Phys. Chem.*, 14, *665–677 (1910).*

[2] F. Haber, *Z. Elektrochem.*, 7, *441448 (1901);* E. Bose, *Z. physik. Chem.*, 34, *726–730 (1900);* E. Bose, *ibid.*, 38, *23–26 (1901);* Bornemann, *Z. Elektrochem.*, 15, 673–679 *(1910); G. N.* Lewis, THIS JOURNAL, 28, *164 (1906).*

[3] N. H. Furman, *ibid.*, 44, 2685–2697 *(1922);* Tilley and Ralston, *Trans. Am. Electrochem. Soc.*, 44, *31 (1923);* A. K. Goard and E. K. Rideal, *Trans. Faraday Soc.*, 19, *740–747 (1924);* W. T. Richards, *J. Phys. Chem.*, 32, *990–1005 (1928).*

Work in this Laboratory has shown[4] that the value and steadiness of the potential of the oxygen electrode are influenced markedly by the flowing of the electrolyte. Further investigations have brought the writers to the belief that these potentials are due largely, if not wholly, to the adsorption on the platinum of ions from the solution; an adsorption potential. The object of this paper is to present this explanation of the anomalous behavior of the so-called oxygen electrode.

Apparatus.—The apparatus used for all the experiments except those under reduced pressure was entirely analogous to that customarily employed for the measurement of hydrogen electrode potentials. Cells having a capacity of about **50** cc. were used with stoppers which provided for gas inlet and outlet, bridge connections and electrode. Bright platinum wire was used for the most part as electrodes, though some measurements were made with platinized wire and both bright and platinized foil. Commercial oxygen was used after being passed through acidified potassium permanganate, dilute sodium hydroxide and distilled water. The cells were supported in a thermostat which was maintained at a temperature of **25** ± 0.02°. The potentials were measured with a Leeds and Northrup student type of potentiometer, and a Leeds and Northrup lamp and scale galvanometer. Readings of potentials were made on neutral, acid and alkaline solutions. These were made using chemicals of "C. P. analyzed" quality. The potentials presented are referred to the standard molal hydrogen electrode, taking the value of the normal calomel electrode equal to **−0.283** volt. They therefore represent the potential of the cell

$$\text{Pt} - O_2\text{, electrolyte, KCl (1 N), } H^+ \text{ (1 } M\text{), } H_2 - \textbf{Pt}$$

For the sake of brevity, readings have been reported at rather long time intervals. About twice as many readings were taken as appear in each table; the complete data are not essential to showing the characteristics of the various runs.

The investigations on the effect of removing dissolved gases from the electrolytes were conducted by means of the apparatus shown in Fig. 1. A water-jet filter pump was employed which reduced the pressure sufficiently to cause boiling of all the solutions used. A manometer, connected in the system, gave an average reading of 18 mm. The connecting bridge between the two cells was filled with a stiff agar jelly made with tenth molar potassium sulfate solution. This was found necessary to prevent sucking out of the conducting medium between the two cells. A similar jelly made up with molar potassium chloride was placed up to the stopcock in the connecting tube of the calomel electrode vessel. The stopcock was kept closed throughout the evacuation. Electrical contact could be readily maintained in this manner and the inconvenience and possible

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[4] Tartar and Wellman, *J. Phys. Chem.*, **32,** 1171–1177 (1928).

source of error associated with evacuation of the calomel electrode vessel were thus avoided.

Adsorption the Cause of the Potential.—The writers propose the following explanation to account for the potential of the oxygen electrode. The platinum preferentially adsorbs ions from the solution and thus produces a potential difference between the electrode surface and the bulk of the solution. To elucidate, let us suppose that there is in solution a uni-univalent salt, the cations of which are adsorbed by the electrode in greater amount than the anions, making the electrode positively charged with respect to the solution. The ions do not form two distinct layers at the surface of the electrode, the "electrical double layer" inference found many times in the literature, but are arranged so that the concentration of each ion gradually changes with increasing distance from the metal until they finally become the same as in the bulk of the surrounding medium. The diagram in Fig. 2 will probably aid in making the conception clearer. Between o and a, the cations are in excess; and between a and d, the anions. From o to d the number of cations is equal to that of the anions, but for a lesser distance o to b, the cations are in excess. The adsorption of ions by the metal produces a potential gradient between the surface of the electrode and the point d, the magnitude and the steepness of which depend entirely upon the excess of cations preferentially adsorbed. For a negatively charged electrode the arrangement of the cations and anions would be interchanged.

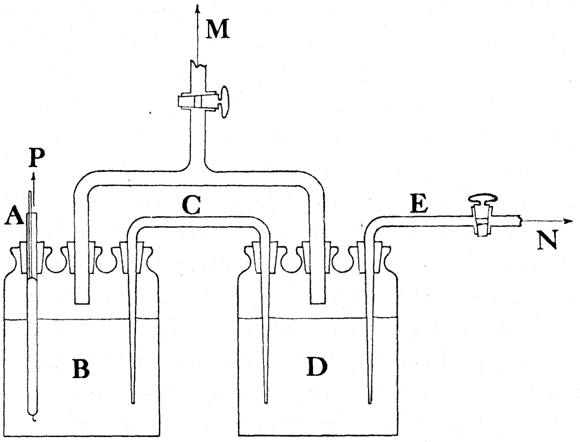

Fig. 1.—A, electrode; B, electrolyte; C, agar-filled bridge; D, KCl, about 1 *M*; E, connecting bridge filled with agar to stopcock; M, to manometer and suction pump; N, to normal calomel electrode; P, to potentiometer.

This concept of the potential of the electrode is consonant with the deductions of Debye and Hückel,[5] Gouy,[6] Powis,[7] McBain,[8] and Burton" regarding the distribution of ions in a Helmholtz double (?) layer.

The effect of the oxygen gas on the potential is due to its influence on the adsorption of ions. When the gas is dissolved in the solution, some oxygen molecules are adsorbed on the surface of the metal, thereby causing a change in the adsorption of ions from the electrolyte.

In support of the above explanation the writers submit the following evidences.

Evidence from **the** Drift of **the** Potential.--One characteristic of the electrode is that the potential changes or drifts with time. The rate of drift depends upon the electrolyte being greater with alkaline than with neutral or acid solutions Furman[3] states, and work in this Laboratory confirms his observations,[4] that the drift is from 30 to 60 millivolts per hour in alkaline solution and from 5 to 10 millivolts per hour in acid solution. Furthermore, the change is in a given direction for a particular electrolyte and is toward a greater potential difference between the electrode and the solution.

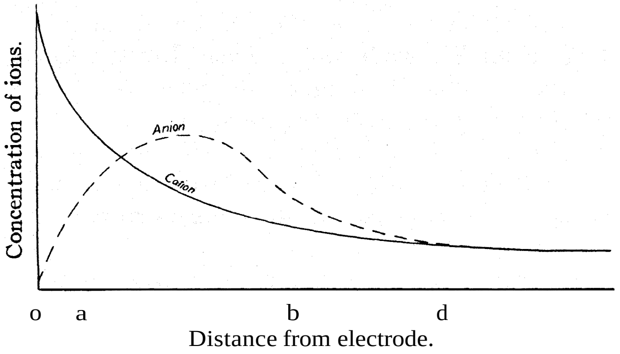

Fig. **2.**

This uni-directional drift may be considered as a consequence of the slow adjustment in the outer fringe of the ionic layer, *i. e.*, of the part b to d, Fig. 2. This is substantiated by the fact that with time, the drift becomes appreciably slower and the potential approaches a steady value. This time element is not surprising when it is considered that the ionic layer throughout which the potential gradient exists is probably many ions deep, and the forces holding the outermost ions in position become very weak.

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[5] Debye *and Hdckel, Physik Z., 24,* 185 (1923).

[6] Gouy, *J. phys.* [4], 9, **457** (1910).

[7] Powis, Trans. Faraday *Soc.,* **11,** 160 (1916).

[8] McBain, J. *Phys. Chem., 28, 706* (1924).

[9] Burton, "Colloid Symposium Monograph," Chemical Catalog Co , New York, 1926, Vol IV, p 13%.

Influence of Movement of Electrolyte upon the Steadiness of the Potential.—It has been shown by Tartar and Wellman[4] that the potential becomes more steady, ceases to drift, when there is a uni-directional flow of the electrolyte past the electrode. The potential becomes fairly constant for a given electrode in a given solution provided the rate of flow remains unchanged. This phenomenon can be explained as being due to the effect upon the distribution of the ions from the surface of the electrode. In the region a, Fig. 2, the distribution is maintained by electrical forces sufficiently great to be but little influenced by the movement of the electrolyte. Forces of less magnitude operate in the region b to d, which are more easily overcome by the movement of the solution. Thus the flow gives a shearing force opposing the electrical forces tending to maintain the potential difference from o to d and the fringe, say b to d, is swept away. This results in a more constant potential and the elimination of the drift.

Effect of Jarring the Electrode and of Small Electric Currents.—With some solutions the potential shifts markedly when the electrode is gently tapped. This effect may be accounted for in the same way as that produced by the movement of the electrolyte. The tapping moves the electrode with respect to the solution, thereby producing a change in the arrangement of the ions, particularly in the outer portion of the ionic layer (b to a).

Difficulty was experienced in reading the potentials in neutral and acid solutions. The potentiometer could be set anywhere within a range of 40 to 60 millivolts and the galvanometer show no deflection if the connecting key were tapped frequently enough. This apparent "balance," obtained both above and below the actual potential, is due to modifications in the ionic layer by the small electric current to and from the electrode when the potentiometer was "off balance."

Evidence from the Effects of Gases Other than Oxygen.—It has been suggested earlier in this paper that the influence of the oxygen gas on the value of the potential is due to the modification of the electrode surface by the adsorption of oxygen molecules. This modification is not limited to oxygen alone but should occur with other gases as well. Accordingly, investigations were conducted with nitrogen and hydrogen.

In the case of hydrogen, a neutral electrolyte was used, *viz.*, a saturated solution of potassium sulfate. The electrode was of bright platinum, which accounts for the difference between the type of readings obtained and that usually associated with the hydrogen electrode. Table I gives a set of readings, together with notations indicating manipulations of the gas and the electrode. The data show that the potential drifted markedly and was extremely sensitive to the effects of jarring and of other disturbances in the immediate vicinity of the electrode. This would indicate that hydrogen gas has a very pronounced modifying influence on the adsorption of ions by the platinum—an indication which is hardly more than would be expected in view of the relatively high adsorption of hydrogen itself on platinum. Hence the potentials are of an electrode which is functioning in part only as a hydrogen electrode, and where the predominating influence is still that of ions adsorbed from solution.

TABLE I

POTENTIAL WITH BRIGHT PLATINUM IN SATURATED POTASSIUM SULFATE IN THE PRESENCE OF HYDROGEN GAS

Time, min.	Potential, volts	Manipulations	Time. min.	Potential, volts	Manipulations
0	−0.368	Hydrogen bubbled in	102	0.367	
10	+ .162		105	.352	Hydrogen bubbled directly on electrode
30	.207	Electrode shaken			
40	.257		107	.382	
50	.182		110	.362	
80	.312		115	.342	Electrode shaken
100	.337	Hydrogen bubbled directly on electrode	130	.427	

The second gas (nitrogen) was chosen because of its inertness and comparatively low adsorption on platinum. By analogy, we expected that the potential with this gas would drift more slowly than with either oxygen or hydrogen. The data, which appear in Table II, seem to bear out this prediction.

TABLE II

POTENTIAL WITH BRIGHT PLATINUM IN SATURATED POTASSIUM SULFATE IN THE PRESENCE OF NITROGEN GAS

Time, minutes	0	5	10	15	35	65
Potential, volts	−0.395	−0.383	−0.338	−0.328	−0.300	−0.386
Time, minutes	95	125	190	310	370	
Potential, volts	−0.278	−0.265	−0.248	−0.223	−0.193	

The readings were continued for periods up to twenty hours without a definite cessation of the drift, though the rate of change became extremely slow. For the first 300–400 minutes the potential seemed to be affected but little by external disturbances, but thereafter became much more sensitive. A similar run was conducted with normal sulfuric acid and nitrogen gas, which gave the same type of results; e. g., at the end of nine hours the potential was still drifting at the rate of 12–13 millivolts per hour.

Evidence from Potentials in the Absence of Gases.—If the suggested interpretation of the effect of gases on this potential is correct, the characteristic drift should exist when no gas is present. To show this, investigations were conducted using the apparatus already described and shown in Fig. 1.

Previous to evacuation, the electrolyte was saturated with the desired gas and readings of potential taken for some time. Oxygen, hydrogen and nitrogen were used. The electrolyte was a saturated solution of potassium sulfate, so that no difficulty arose due to changes in concentration during the course of evacuation. Table III gives a summary of these results.

TABLE III

POTENTIALS WITH BRIGHT PLATINUM IN SATURATED POTASSIUM SULFATE DURING REMOVAL OF DISSOLVED GASES

Time, min.	Potential, volts (satd. with oxygen)	Potential, volts (satd. with hydrogen)	Potential, volts (satd. with nitrogen)
0	. .	. .	−0.179[d]
20	. .	. .	−0.174
30	−0.377[a]	+0.339[c]	.166[b]
50	.381	.427[b]	.164
80	.381[b]	.172	.161
100	.372	.132	.160
130	.340	.107	.158
160	.338	.008	
220	.336	−0.083	
280	.331	.113	
340	.324 .278 (5 5 hours)	157 .163 2 hours	

[a] Oxygen bubbled in. [b] Bvacuation begun. [c] Hydrogen bubbled in. [d] Nitrogen bubbled in for seven hours.

These data indicate that the cessation of the drift appears to be in no way hastened by the removal of dissolved gases from the electrolyte. Similar work of more limited extent was performed with saturated oxalic acid as the electrolyte with confirming results.

Evidence from Potential with "Immobile" Electrolytes.—If the ionic layer is of the thickness suggested, it should be possible to stabilize it by making the electrolyte less mobile or else by packing a sufficiently finely divided material about the electrode.

An attempt to steady the potential in this way was made by imbedding the electrode in finely powdered silicon dioxide covered with the electrolyte. Bright platinum electrodes were used. Oxygen was bubbled continuously through the electrolyte with the tip of the gas inlet tube below the surface of the powdered material and at a distance of not more than 8 mm. from the electrode. Neutral, acid and alkaline solutions of varying normalities were used in order to determine the dependence of the steadiness of the potential upon the concentration. In general, the more concentrated solutions gave the more stable potentials but the difference in the type of readings was not sufficiently pronounced to warrant the inclusion of all the data. Hence, potentials for only one concentration of each electrolyte will be reproduced. In each case a series of readings in the same electrolyte and without the silicon dioxide was taken simultaneously and the results of these are also given in Table IV.

TABLE IV

POTENTIALS WITH BRIGHT PLATINUM IN NEUTRAL, ACID AND ALKALINE ELECTROLYTES WITH AND WITHOUT SILICON DIOXIDE POWDER

Time, min.	Potential in electrolyte without powder, volts	Potential in electrolyte with SiO_2 powder, volts	Time, min.	Potential in electrolyte without powder, volts	Potential in electrolyte with SiO_2 powder, volts	Time, min.	Potential in electrolyte without powder, volts	Potential in electrolyte with SiO_2 powder, volts
	M/10 K_2SO_4			*N* H_2SO_4			*N* KOH	
10	−0 490	−0 516	10	−0 814	−0 696	10	+0 159	+0 119
30	.458	,515	20	.818	.683	30	.153	.116
75	.435	.516	60	.816	.683	100	.146	.114
105	,425	516	140	825	6	130	.144	.113
120	.433	.515	210	.811	.683	160	.142	.113
165	,428	.518				210	.140	.113
190	.430	.518						
300	.432	.521						

The results show that in all cases the addition of the powdered material had a stabilizing influence, more so in the alkaline and acid solutions than in the neutral. The above experiments were repeated with a coarser medium employed as a stabilizer, namely, Ottawa sand. It was found that this material had the desired effect in the alkaline and acid solutions but was of little assistance in the neutral electrolyte. Three sets of readings are given in Table V. It will be noted, however, that while the presence of the sand does not render the potential with the neutral electrolyte steady, it does stop the tendency to drift continuously.

TABLE V

POTENTIAL WITH BRIGHT PLATINUM IN NEUTRAL, ALKALINE AND ACID ELECTROLYTES IN COARSE SAND

Time, min.	Potential in *M*/10 K_2SO_4, volts	Potential in *N* KOH, volts	Potential in *N* H_2SO_4, volts
10	−0.602	+0.103	−0.730
20	.592	.106	.690
80	.583	.103	.701
100	.581	.100	.702
130	.583	.100	.702
160	.581	.100	.702
180	.582	.098	.702
210		.098	.702

The effect of powdered silicon dioxide on the potential with *platinized* platinum electrodes in alkaline and acid solution was observed; it was found that with this type of electrode surface the amount of stabilization produced in this manner was negligible.

Further experiments were made by placing bright platinum electrodes in agar jelly containing the electrolyte; tenth molar potassium sulfate and tenth normal sulfuric acid were used. The potentials were very steady and did not drift. Because of the indefinite nature of the agar jelly, it is not possible to say that the steady potentials were due wholly to the stabilization of the ionic layer.

Evidence from the Effect of Substances Reducing Interfacial Tension.—Another method for showing the role played by adsorbed ions in producing these potentials was based on the effect obtained when the interfacial tension between the electrode and the electrolyte was reduced. Two types of substances were employed; one polar and the other non-polar. These were potassium pelargonate and amyl alcohol, respectively. Since the former would interact with the acid solution, readings were taken with it only in neutral and alkaline electrolytes. The data appear in Table VI. The concentration of the pelargonate was about 0.25 g. per 100 cc. of electrolyte.

TABLE VI

POTENTIALS WITH BRIGHT PLATINUM IN NEUTRAL AND ALKALINE ELECTROLYTES WITH POTASSIUM PELARGONATE

Time, minutes		15	75	135	195	250	255
Potential, volts	in $N/10 K_2SO_4$	−0.566	−0.566	−0.566	−0.566	−0.566	−0.566
	in $N/10$KOH	+0.181	+0.203	+0.205	+0.205	+0.205	+0.205

In the case of amyl alcohol, all three electrolytes were used, and were made about 1% with respect to the amyl alcohol. Table VII contains readings taken in this manner.

TABLE VII

POTENTIALS WITH BRIGHT PLATINUM IN NEUTRAL ACID AND ALKALINE ELECTROLYTES WITH AMYL ALCOHOL

Time, min.	**Potential in $N/10$ K_2SO_4, volts**	**Potential in $N/10$ H_2SO_4, volts**	**Potential in $N/10$ KOH, volts**
10	−0.561	−0.752	+0.154
60	.558	.749	.151
90	.554	.750	.148
200	.550	.750	.147
300	.549	.751	.146

The experiments with amyl alcohol were repeated with platinized platinum with even more gratifying results; *e. g.*, in the case of sulfuric acid ($N/10$) the potential showed no change whatever, after the first twenty minutes, during 500 minutes of observation.

Summary

1. The behavior of the oxygen electrode has been explained as being due largely to the adsorption of ions; an adsorption potential.
2. Experimental evidence has been presented to support this explanation.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 236]

SOME ELECTROMOTIVE FORCE MEASUREMENTS WITH CALCIUM CHLORIDE SOLUTIONS

BY GEORGE SCATCHARD AND RALPH F. TEFFT[1]

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The chemical potential, or partial molal free energy, of sodium or potassium chloride in a mixture of ethyl alcohol and water varies with changing solvent as should be expected if the deviation from ideality were due entirely to electrostatic effects. The very different behavior of hydrogen chloride may be explained simply by the existence of the hydrogen ion in solution in the form of the monohydrate.[2] So it is of interest to study calcium chloride, which has a heavily solvated solid phase in equilibrium with its solution in either solvent. Measurements were made of the electromotive force at 25° of the cell Ag, AgCl, $CaCl_2$(I), $CaHg_x$, $CaCl_2$(II), AgCl, Ag (double cell). Such measurements in aqueous solution have been published by Lucasse[3] and, since the presentation of the thesis on which this paper is based, by Fosbinder.[4] To study more closely the behavior of the amalgam electrodes, measurements were also made on the cell $CaHg_x$, $CaCl_2$, AgCl, Ag (single cell). It was expected that the chief difficulty would be due to chemical action at the amalgam electrode and that alcohol would be less reactive than water, so that a technique which proved satisfactory for aqueous solutions would work well in the alcohol mixtures. The expectations were not realized. Successful determinations were made in water, and fairly accurate ones in 46% (25 mole %) alcohol, but the behavior with 72% (50 mole %) alcohol was so different that no determinations could be made and no attempt was made to work at higher alcohol concentrations.

Apparatus and Materials

The double cell was essentially the same as that of MacInnes and Beattie[5] except that the amalgam droppers were bent into a U shape and were about 5 mm. in diameter. The single cell was half the double cell, with an amalgam dropper having a single outlet. Droppers were used with tips varying from 1 to 11 mm.

Measurements were made in an atmosphere of hydrogen. Tank hydrogen was passed over copper at about 300°. That which was to be used over the solutions was then bubbled through some solution of the same composition; that which was to be used over the amalgam was dried by passing over calcium chloride and phosphorus pentoxide.

The water used for all solutions was twice-distilled "conductivity" water. Com-

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[1] From a thesis submitted in May, 1928, by Ralph F. Tefft in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Scatchard, THIS JOURNAL, 47, 2098 (1925).

[3] Lucasse, *ibid.*, 47, 743 (1925).

[4] Fosbinder, *ibid.*, 51, 1345 (1929).

[5] MacInnes and Beattie, *ibid*, 42, 1123 (1920).

mercial alcohol was refluxed with lime for several days and then distilled. The middle portion was redistilled from aluminum amalgam, and the water content was determined from the density.

Calcium carbonate was prepared by precipitation from a solution of c. p. calcium chloride with c. p. ammonium carbonate, and was washed until free from chlorides. The stock solution of calcium chloride was prepared by the action of constant-boiling hydrochloric acid on an excess of this calcium carbonate. After the action had subsided, hydrogen was passed through for several hours. The hydrogen-ion concentration of this solution was between the methyl orange and phenolphthalein neutral points; the calcium chloride concentration was determined gravimetrically as silver chloride. The solutions of calcium chloride were prepared by weight dilution of this stock solution with water or with water and alcohol. A stream of hydrogen was passed through the diluted solution for five or ten minutes to remove any air admitted during the handling.

Mercury was purified by being passed eight times through a tower containing dilute nitric acid and mercurous nitrate, and then twice distilled in a current of air under reduced pressure. In recovering mercury from used amalgams, the distillations were omitted. The calcium amalgam, which contained 0.02–0.05% of calcium, was prepared by the electrolysis of the stock solution of calcium chloride with a mercury cathode. It was then rinsed, dried and stored in an evacuated pyrex container.

The silver–silver chloride electrodes were prepared by the method of MacInnes and Beattie,[5] and chloridized in the solution in which they were to be used except that for solutions more concentrated than 0.3 M they were chloridized in 0.1 M solution, because electrolysis in the more concentrated solutions gave a compact non-conducting layer. At least 5 electrodes were prepared in each case, and that one used which was nearest the average in electromotive force. No electrode was considered in the average which differed from the others more than 0.05 mv.

The apparatus was placed in a water thermostat maintained at 25.00 * 0.01°. The potentiometer was a Leeds and Northrup Type K with an unsaturated cadmium sulfate reference cell. This cell was frequently checked against a series of saturated cadmium sulfate cells.

Measurements with the Single Cell

The cell $CaHg_x$, $CaCl_2$, AgCl, Ag was used with approximately 0.02% calcium amalgam and 0.1 M calcium chloride in water with a series of U-shaped amalgam droppers having tips about 1, 3, 7 and 11 mm. in diameter. The rate of flow was varied from less than one drop per second to a continuous stream, and the electromotive force was also measured after flow was stopped. The electromotive force after stopping the flow was practically independent of the size of the tip. It decreased one or two-tenths of a millivolt per minute.

The 1-mm. dropper showed considerable fluctuation while the amalgam was flowing, and the electromotive force with streaming amalgam was 6 mv. less than with no flow. The 7-mm. dropper was much steadier and decreased only 2.5 mv. The 3-mm. dropper was intermediate in its behavior. The 11-mm. dropper behaved quite similarly to the 7 mm. one except that a bubble of hydrogen which formed on the surface was not carried away even with rapid flaw and, presumably for that reason, the results were more erratic, Measurements were also made on the cell $ZnHg_x$, $ZnCl_2$, AgCl, Ag with about 0.05% zinc amalgam and about 0.1 *M* aqueous $ZnCl_2$, and with a 5-mm. dropper. The electromotive force at 10 drops per second (almost continuous flow) was 0.5–0.6 mv. less than that immediately after the flow was stopped.

With the double cells the rate of flow was varied greatly, keeping the two rates as nearly equal as possible. That value was accepted which held over a large range of rates. The changes noted were probably due to small differences in the two rates, for there was no trend of the difference with the rate and visible differences between the two rates did give large changes in electromotive force. This technique was satisfactory with aqueous solutions if the rate was not too great (fast streaming) and the amalgam concentration not too small (less than 0.015%).

The direction of the change in electromotive force with changing rate of flow is surprising. Chemical action at the electrode would decrease the calcium concentration and increase that of calcium ion, and so decrease the electromotive force. The effect would be smaller the more rapid the flow, so that rapid flow should give the largest electromotive force.

The only cause which occurs to the authors which would give an electromotive force decreasing with the rate, and decreasing the more rapidly at high rates, is failure to obtain equilibrium between the surface and the bulk of the amalgam. If the interfacial tension decreases with increasing calcium content of the amalgam, the calcium will be adsorbed at the interface, and calcium will have a smaller chemical potential in a fresh surface than in the bulk liquid from which it is formed. The resulting decrease in electromotive force should be greater the more rapid the flow. This explanation also accounts for the fact that the difficulty is greater the more dilute the amalgam, for the relative unsaturation would be greater, but that it is practically independent of the salt concentration.

No measurements have been made of the interfacial tension between calcium amalgams and solutions of calcium salts. Schmidt[6] and Oppenheimer[7] have measured the surface tensions of amalgams in *vacuo*. The first found that lithium and the alkaline earth metals increase the surface tension of mercury greatly and that zinc does a little, while sodium and potassium give large decreases. The second found that lithium decreases the surface tension even more than sodium, and that calcium gives a considerable decrease. Meyer[8] measured the interfacial tension of zinc and the alkali amalgams against aqueous solutions of their salts. He found that all decrease the interfacial tension, lithium enormously. His results parallel those of Oppenheimer. The effect is in the proper direction to account

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[6] Schmidt, *Ann. Physik*, **39**, 1108 (1912)

[7] Oppenheimer, *Z anorg. allgem Chem*, **171**, 98 (1928).

[8] Meyer, *Z. physik. Chem.*, **70**, 315 (1910).

for our observations with zinc amalgam and, if the parallelism to Oppenheimer's results may be extended to calcium amalgam, it should give a much larger effect in the same direction. This is also in accord with our observations.

Our double cell technique gave measurements in 46% alcohol reproducible only to 0.5 mv. instead of 0.1–0.2 mv., but they still seemed fairly satisfactory. With 72% alcohol, however, the discrepancies were so great that measurements were again attempted with the single cell, using a 5-mm. dropper. Two runs were made. In the concentrated run the amalgam concentration was about 0.04% and the salt concentration about 0.2 M. In the dilute one the amalgam was about 0.01% and the salt about 0.02 *M*. In both cases a scum, probably calcium hydroxide, formed on the surface of the amalgams. The fluctuations were very large, particularly at the slower rates of flow with the concentrated amalgam. The electromotive force increased with rate of flow, about 35 mv. for the concentrated and about 45 for the dilute. In both cases the increase was large even after the flow was continuous.

Since the effect of the rate of flow is so enormous, there is little chance of maintaining the two rates of flow in the double cell near enough equal to give significant results. Measurements with aqueous solutions on one side and alcoholic solutions on the other are quite out of the question since the electromotive force is changed in opposite directions by changing the rate. For this reason work on alcoholic solutions was discontinued.

Wolfenden and his co-workers[9] made measurements with a single jet electrode with sodium amalgam and a methyl alcoholic solution of sodium chloride. With 0.04% amalgam they found that the electromotive force increased about 4 mv. when the rate of flow was increased, and that the effect was independent of the salt concentration They concluded that the cause was not chemical action because the increase persisted with large rates of flow. With 0.003% amalgam they found that increasing the rate of flow sometimes increased the electromotive force somewhat more than with the concentrated amalgam and sometimes gave a decrease of the same order of magnitude.

The argument of these authors against chemical action as the cause of the effect of changing rate applies equally to our results. If adsorption is the cause, it must be adsorption of the metal ion, and it is surprising that they found practically no change for a hundred-fold increase of salt concentration. The difficulties of any explanation are enhanced by the magnitude of the effect which must be explained, for the change in electromotive force with the alcoholic calcium chloride solutions corresponds to a twenty- or thirty-fold increase of calcium ion. That such a change can result from chemical action, adsorption or the combination of the two is scarcely to be expected.

[9] Wolfenden, Wright, Kane and Buckley, Trans. *Faraday Soc.*, **23,** 491 (1927).

Measurements with the Double Cell

Since the accuracy of measurement decreases for very dilute solutions, a 0.1 M solution in water was chosen as comparison standard. Table I gives the results of the measurements with aqueous solutions. The first column gives the exact concentration of the reference solution (in moles per 1000 g. of solvent); the second column, the concentration of the second solution; the third column, the measured electromotive force; and the fourth column gives this value minus the value calculated from the Debye–Hückel equation with the constants given below. In Fig. 1 these deviations are shown graphically together with the corresponding deviations of the measurements of Lucasse and of Fosbinder, both of whom used a 0.01 M solution as reference standard. The measurement of Fosbinder at 0.0897 M and all his measurements above 1 M are omitted because the deviations are larger than the scale of the figure. The average deviation of our measurements is 0.41 mv.; below 1.0 M that of Lucasse is 0.71 mv.,

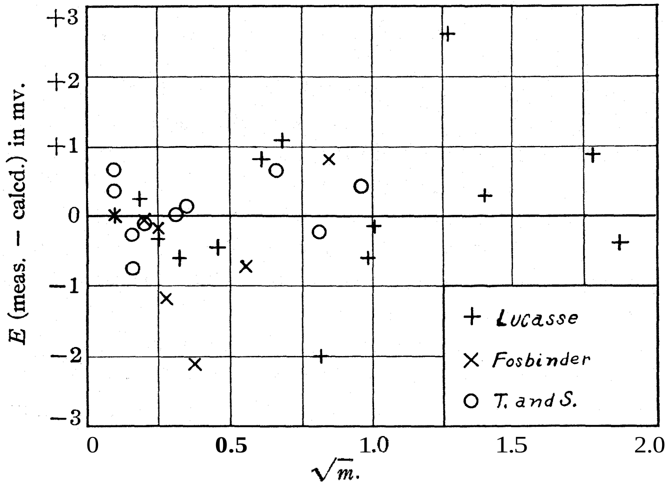

Fig. 1.—Electromotive force of calcium chloride cells.

TABLE I

ELECTROMOTIVE FORCE OF CALCIUM CHLORIDE CONCENTRATION CELLS IN WATER

m_1	m_2	E(meas.)	E(meas. − calcd.)
0.09989	0.009921	0.0761	+0.0004
.09978	.010509	.0742	+ .0007
.10041	.02594	.0439	− .0003
.09983	.02758	.0412	− .0007
.09989	.04113	02892	− .00010
.09993	.12634	− 0078	+ .0001
.10029	.4420	− 0558	+ .0007
09968	.6589	− 0768	− .0002
.10056	.9301	− 09615	+ .00043

and of Fosbinder 1.45 mv. The agreement between these independent observations gives some assurance that the electromotive force of the calcium chloride concentration cell with aqueous solutions does measure the free energy of transfer of the salt.

A concentration cell such as [Ag, AgCl, $CaCl_2$(I), $CaHg_x$], $CaCl_2$(II), AgCl, Ag in which the composition of solution (I) is kept constant during a series of measurements while solution (II) is varied may be treated as though that portion of the cell in brackets were a single electrode. This treatment is particularly convenient when the variation in solution (II) is a change in the solvent. By the theory of Debye and Hückel, the electromotive force, E, of such a cell is given by

$$E = E_0 - k \log \frac{m}{1 + wm} + \frac{A\sqrt{c}}{1 + \alpha\sqrt{c}} - \beta c - k' \qquad (1)$$

m is the number of moles of salt per kilogram of solvent, c the moles per liter of solution (both in solution 11), and w is one-thousandth of the average molecular weight of the solvent multiplied by the number of ions in one mole of salt.[10] E_0 depends upon the temperature, the nature of the solvents on the two sides and on the concentration of solution (I). The computation of the numerical constants need not be repeated here, but it is sufficient to say that for a bi-univalent electrolyte at 25° k is 0.088725 volt and k' is 0.01781 volt; if the solvent is water, w is 0.054, A is 0.1550 volt, and $\alpha = 0.568$ a, where a is the diameter of the mean collision sphere of the ions in Ångström units; in 25 mole % alcohol, w is 0.075, A is 0.310 volt, and a = 0.716 a. β is a function of the solvent composition and the temperature which must be determined from the data.

If the solvent is the same on the two sides, the constants a and β may be determined from two measurements, and E_0 is given from the fact that E must be zero when the two concentrations are equal. If the solvents are different, three measurements are necessary to determine the three constants. Equation 1 was used to determine the small correction necessary because m_1 was not exactly 0.1 M, and to determine the difference in E_0 between our measurements and those of the other workers, who used different standard concentrations.

For aqueous solutions the volume concentrations were computed by the equation $c/m = 0.99707 - 0.0214\,m - 0.0019\,m^2$, and the constants used are $a = 2.1$, which corresponds to $a = 3.70$, $\beta = 0.04$ volt, and $E_0 = -0.13217$ volt when $m_1 = 0.1$ M. Values of γ computed with these constants are given in the following paper.[11]

The results in 25 mole per cent, alcohol, with solution I in water, are given in Table II. The first column gives the concentration of the aqueous solu-

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[10] For any one solvent, then, $m/(1 + wm)$ is proportional to the mole fraction of either ion.

[11] Scatchard and Tefft, THIS JOURNAL, 52, 2272 (1930).

TABLE II

ELECTROMOTIVE FORCE OF CALCIUM CHLORIDE CELLS IN 25 MOLE PER CENT. ALCOHOL

m_1	m_2	ρ_2	E	E_0
0.1102	0.01316	0.91995	−0.0081	−0.2219
.1003	.1192	.92798	− .0785	− .2278
.1003	.9712	.99126	− .16295	− .2244

tion, the second that of the alcoholic solution in moles per kilogram of solvent, and the third column gives the measured density, from which the volume concentrations were calculated. The fourth column gives the measured electromotive force, and the fifth E_0 calculated from Equation 1. Giving a the same value as in water, α is 2.65, and the data are fitted best by taking $\beta = 0.05$ volt. The average E_0 is –0.2247 volt. The average deviation is large, 2 millivolts, but this is not surprising in view of the extreme difficulty with 50 mole per cent. solutions.

According to Debye's theory of salting out, etc.,[12,2] the change in E_0 with changing solvent should depend upon the molecular weights of the two solvents, their dielectric constants, and the electrical radius of the ions, b, according to the equation (for a bi-univalent electrolyte)

$$E_{01} - E_{02} = 0.088725 \log \frac{M_2}{M_1} + \frac{21.50}{b}\left(\frac{1}{D_2} - \frac{1}{D_1}\right) \qquad (2)$$

For water and 25 mole per cent. ethyl alcohol, the first term is 0.01266 volt, leaving 0.0799 volt for the electrical term. The coefficient of l/b is 0.1605 volt. This gives b = 2.0 Angstrom units, which agrees with the value computed from the salting out of H_2, O_2 and CO_2.[13]

Summary

The electromotive force of the cell Ag, AgCl, $CaCl_2$ (0.1 M, aq.), $CaHg_x$, $CaCl_2$ (m), AgCl, Ag has been measured at 25° with m varying from 0.01 to 1.0 in water and in 25 mole per cent. ethyl alcohol, and the Debye theory has been applied to the results.

With aqueous solutions the potential of the calcium amalgam electrode decreases slightly with increasing rate of flow, probably because of adsorption of calcium at the interface.

With water–alcohol mixtures the potential increases rapidly with increasing rate of flow, so that accurate measurements are not possible when the alcohol concentration is large.

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[12] Debye and MacAuley, *Physik. Z.*, **26**, 22 (1925).

[13] Scatchard, *Trans. Faraday Soc.*, 23, 454 (1927).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 237]

ELECTROMOTIVE FORCE MEASUREMENTS ON CELLS CONTAINING ZINC CHLORIDE. THE ACTIVITY COEFFICIENTS OF THE CHLORIDES OF THE BIVALENT METALS

BY GEORGE SCATCHARD AND RALPH F. TEFFT[1]

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The behavior of zinc chloride in solution is of interest as it represents an intermediate step in the transition from typical strong electrolytes, such as the alkaline earth chlorides, to salts like cadmium chloride in which ion association shows an important effect. A few measurements on the cell Zn, $ZnCl_2$ (m), AgCl, Ag have been made at 0° by Jahn,[2] and several in very dilute solutions at 25° by Horsch.[3] We have made a series of measurements on the cell ZnHg (2 phase), $ZnCl_2$ (m), AgCl, Ag at 25° in which m was varied from 0.003 M to 1.48 M.

Experimental Methods

A solution of C. P. sodium carbonate was added to a solution of C. P. zinc chloride in water. The resulting precipitate was washed free from chlorides and dried at about 300° overnight, leaving a product largely zinc oxide. This was mixed with purified hydrochloric acid and boiled until no more would dissolve. The concentration of this stock solution was determined by a gravimetric chloride analysis, and the solutions used in the cells were prepared from it by weight dilution.

The stock solution was saturated with zinc oxide, and on dilution a small amount of precipitate always formed. According to Driot[4] the solid phase is $4ZnO{\cdot}ZnCl_2{\cdot}6H_2O$ at these concentrations of zinc chloride, and the solubility is given by $m_{ZnO} = 0.005\ m^2_{ZnCl_2}$. This excess concentration affects only the zinc electrode, so that the correction is 0.03 log (1 + 0.005 m), which is less than 0.1 mv. even for the most concentrated solution studied. All measurements are so corrected, however. The two most concentrated solutions, which were prepared from a more concentrated stock solution than the others so that precipitation was considerable, were each analyzed for chloride.

The zinc amalgam was prepared by the electrolysis of the stock solution, acidified with a small amount of hydrochloric acid, between a C. P. zinc anode and a mercury cathode. After the electrolysis the amalgam was washed, dried and stored in a pyrex

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[1] The experimental work was presented in May, 1928, by Ralph F. Tefft in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Jahn, *Wied. Ann.*, 28, 21 (1886).

[3] Horsch, THIS JOURNAL, 41, 1787 (1919).

[4] Driot, *Compt.* rend., 150, 1427 (1910).

container under hydrogen. To fill the cells the amalgam was heated until it was practically one phase and withdrawn through a capillary stopcock.

The purification of other materials and the preparation of the silver–silver chloride electrodes, chloridized in the solution in which they were to be used except as noted below, the thermostat and the electrical apparatus were the same as in previous work.[5]

The electrode vessel was triplicate. Each section was shaped like an inverted h. The long arm contained the amalgam and had a platinum wire sealed through the bottom. A tube which delivered hydrogen just above the amalgam surface passed through a rubber stopper at the top. The silver chloride electrode was supported in a rubber stopper in the short arm. The three long arms were connected in a row by two series of tubes, one below and one above the liquid–gas interface. The middle section had a second side arm for the escape of hydrogen.

The nine possible electrode combinations were measured in each case except for the most dilute solutions, where the resistance was too high to permit accurate measurements from one end cell to the other. Each cell was observed for at least six hours after it was placed in the thermostat, with the hydrogen flowing continually, although the electromotive force never changed more than 0.1 mv. after the first half-hour, even in one case which was observed for several days. In the 0.003 and 0.02 M solutions one zinc electrode, and in the 0.008 M solution one silver chloride electrode, gave results so different from the other two that they were not considered. Excepting these, the average deviations for a given solution were 0.02–0.07 for all but the most dilute solution, where it reached 0.22 mv. from the average for two fillings, for one of which the silver chloride electrodes were chloridized in a more concentrated solution.

The effect of air was studied with the 0.09 M solution. The passage of air over the amalgam electrodes for twenty minutes caused a decrease of 3–5 mv. in the electromotive force, but the electromotive force began to increase as soon as the flow was stopped and after seven hours had returned to its initial value, which was not further changed by passing through hydrogen. The passage of air caused a scum to be formed on the amalgam surface. Evidently the oxygen removes zinc from the dilute amalgam to form zinc hydroxide, which is precipitated, so that the net effect is the decrease of the zinc concentration in the amalgam. As the amalgam returns to equilibrium, the electromotive force recovers. This action probably accounts for the fact that Horsch,[3] who did not eliminate oxygen, could not prepare reproducible amalgam electrodes.

Measurements

The results of our measurements are given in Table I. The first column

TABLE I

ELECTROMOTIVE FORCE AT 25° OF THE CELL, ZnHg (2 PHASE), $ZnCl_2$ (m), AgCl, Ag

m	E	E_0''	(Eq. 2)
0.002941	1.1983	0.9915	−0.00182
.007814	1.16502	.99586	− .00088
.01236	1.14951	.99800	− .00089
.02144	1.13101	1.00070	− .00063
.04242	1.10897	1,00492	− .00004
.09048	1.08435	1.00940	+ .00018
.2211	1 05559	1.01480	+ .00012
.4499	1.03279	1.01893	− .00020
.6404	1,02206	1.02143	− .00003
1.4802	0.99784	1,02789	− .00004

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[5] Scatchard and Tefft, THIS JOURNAL, 52, 2265 (1930).

gives the molality, the second the measured electromotive force and the third E_0'' defined by the equation

$$E_0'' = E + 0.088725 [\log m - \log(1 + 0.054 m)] + 0.01781$$
$$= E_1 - 0.088725 \log f \qquad (1)$$

E_0'' differs from the E_0' of Lewis and Randall only by the addition of the third term, which relates the measurements to Raoult's law rather than to the assumption that the activity is proportional to the molality in an ideal solution. $0.01781 = 0.088725 \log 2^{2/3}$ serves to change from unit concentration of salt to unit mean concentration of ions. The last column gives the deviations of the measured values from those calculated by the Debye–Hückel equation for varying dielectric constant

$$E_0'' = 0.98625 + \frac{0.155\sqrt{c}}{1 + 3.5\sqrt{c}} + 0.0042c \qquad (2)$$

The values of c for these computations were determined from the densities in the "International Critical Tables," using the equation

$$\frac{c}{m} = 0.99707 - 0.0134\, m - 0.0129\, m^2 + 0.0288\, m^3$$

From 0.04 to 1.48 M the deviations are not more than 0.2 mv., which is probably as small as could be expected. For the more dilute solutions, however, the deviations become very large, and the value of E_0 obtained by this method, 0.98625 v., is certainly too high.

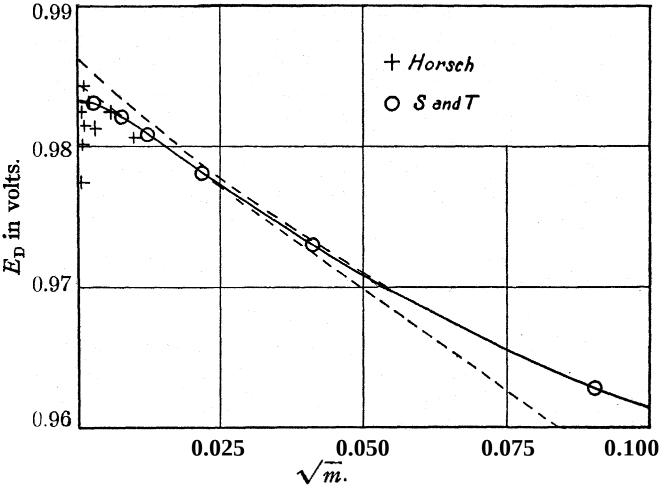

Fig. 1.—Electromotive force of zinc chloride cells.

We have followed the method of Hitchcock[6] in Fig. 1, and plotted

$$E_D = E_0'' - 0.155\sqrt{c} \qquad (3)$$

against the concentration. If the Debye–Hückel equation is approached at small concentrations, E_D should approach a straight line asymptotically

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[6] Hitchcock, This journal, 50, 2076 (1928).

at zero concentration. The upper broken line is that of Equation 2, the lower broken line is a straight one through the points at **0.008, 0.012** and **0.02** M. The point at **0.003** M is well below the line and indicates an inflection in the curve. It would be dangerous to insert an inflection based upon a single measurement, the least accurate of the series, and the measurements of Horsch are too scattered to aid in the extrapolation. However, the points through which the line is drawn fall upon it *too **well*** in view of the deviation at the next higher concentration, so that these points themselves indicate an inflection. Accurate measurements at lower concentrations, to which our technique is not adapted, are to be desired. We believe that the evidence just given and the theoretical considerations which follow justify the inflection, and make the extrapolation along the full curve the most probable.

Chlorides of Other Bivalent Metals

The electromotive force measurements with the alkaline earth chlorides extend only to hundredth molal, so they are not useful for the comparison of the behavior in very dilute solutions. The freezing-point measurements of Hall and Harkins[7] on barium chloride up to **0.1** M are fitted within the accuracy with which they are expressed (one unit in the last place) by the Debye–Hückel equation for constant dielectric constant, assuming that at this dilution $c = m$, with **a** $=$ **4.81** Å.

$$\Theta = 1.858\, \nu\, m \left\{1 - \frac{3.445\, z_1z_2}{x^2a}\left[1 + x - \frac{1}{1+x} - 2 \ln (1 + x)\right]\right\} \qquad (4)$$

ν is the number of ions from one molecule of salt, z_1 and z_2 are their valences, $x = \mathbf{0.3242\,a}\sqrt{\mu}$, μ is the ionic strength, and a the mean effective diameter in Angstrom units. This corresponds to

$$-\log \gamma = \frac{0.485\, z_1z_2\, \sqrt{\mu}}{(1 + x)} \qquad (5)$$

The numerical constants are limited, of course, to aqueous solutions,

At **0.01** M this gives $\gamma = \mathbf{0.737}$, which may be compared with the value 0.716 obtained by Lewis and Randall from the same measurements and to the value **0.724** which we compute, in accord with earlier computations,[8] from the electromotive force measurements of Lucasse at 25°.[9] The difference between our values at 0° and at 25° is in the direction to be expected. It appears that there is no inflection for barium chloride. Strontium and calcium chlorides have larger positive deviations from the limiting law above **0.01** M and should have less tendency to irregularities at smaller concentrations.

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[7] Hall and Harkins, THIS JOURNAL, 38, 2658 (1916).

[8] Harned and Åkerlöf, *Physik. Z.*, 27,411 (1926); Jones and Dole, THIS JOURNAL, 51, 1073 (1929).

[9] Lucasse, *ibid.*, 47, 743 (1925).

The measurements of Carmody[10] on lead chloride and those of Horsch[3] and of Lucasse[11] on cadmium chloride indicate considerable curvature in dilute solutions when E_D is plotted against the concentration. Figure 2 shows $E_D - E_0$ for these salts and for barium and zinc chlorides plotted against the square root of the concentration. The broken line is the Debye–Hückel limiting law. The values for cadmium and lead chlorides in dilute solutions appear to lie on straight lines. For cadmium chloride the slope of this line is greater than that of the broken line, so that extrapolation along this curve would give a limiting slope more than twice the theoretical; lead chloride would give a value about 30% too high.

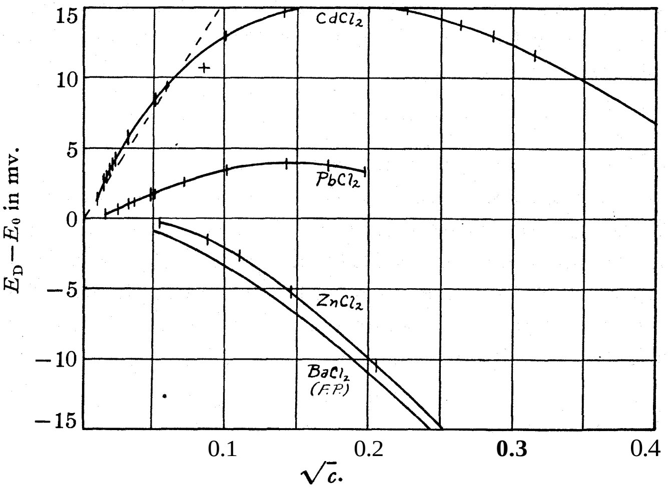

Fig. 2.—Electromotive force of chlorides of bivalent metals.

The Effect of Incomplete Ionization

Since cadmium chloride is certainly not completely ionized and the other salts may not be, the effect of incomplete dissociation on this method of treatment was studied. The effect of the formation of neutral molecules or more complicated ions increases too rapidly with the concentration to resemble the experimentally measured effects, but the formation of the primary ion is capable of explaining the measurements.

It is necessary to distinguish between those quantities computed from the true concentration of the ions, and those computed in the customary way by assuming complete ionization. To the latter we will give the ordinary symbols, while the former will be distinguished by primes. Thus f'_{21} is the true mean activity coefficient of a bi-univalent electrolyte. In calculating the activity coefficients we have assumed that all ions have the size found for barium chloride from the freezing points, that the terms

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[10] Carmody, This Journal, 51, 2905 (1929).

[11] Lucasse, *ibid.*, 51, 2597 (1929).

linear in the concentration are zero, and that the concentration of each species in moles per liter is 55.5 times its mole fraction, a quantity which is designated by the chemical symbol in parentheses. If μ is the ionic strength in these units

$$-\log f'_{21} = \frac{\sqrt{\mu'}}{1 + 1.56\sqrt{\mu'}} \quad \text{and} \tag{6}$$

$$-\log f'_{11} = \frac{0.5\sqrt{\mu'}}{1 + 1.56\sqrt{\mu'}} \tag{7}$$

Given the reaction $MX^{++} \rightleftharpoons M^{++} X^{-}$

$$K = \frac{(M^{++})\,(X^{-})}{(MX^{+})}\,\frac{f'^{3}_{21}}{f'^{2}_{11}} \tag{8}$$

Combining (6), (7) and (8)

$$\log \frac{(M^{++})\,(X^{-})}{(MX^{+})} = \log K + \frac{2\sqrt{\mu'}}{1 + 1.56\sqrt{\mu'}} \tag{9}$$

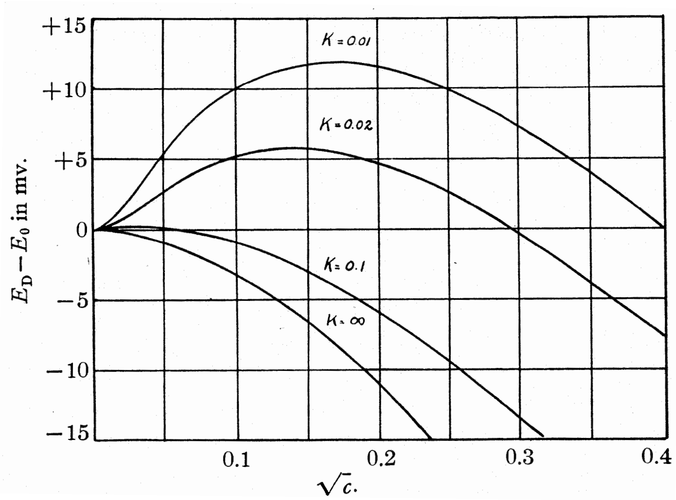

Fig. 3.—Effect of incomplete dissociation on electromotive force of 2−1 salts.

We also have the equations

$$\mu' = 3(M^{++}) + (MX)^{+} \tag{10}$$

$$(X^{-}) = 2(M^{++}) + (MX^{+}) = \mu' - (M^{++}) \tag{11}$$

For a given value of K these equations can be solved without much difficulty if μ' be taken as the independent variable, and

$$= 3[(M^{++}) + (MX^{+})]\ \frac{1 + 0.054\left[(M^{++}) + \frac{2}{3}(MX^{+})\right]}{1 + 0.054\ [(M^{++}) + (MX^{+})]^{3}}, \text{ and} \tag{12}$$

$$f_{21} = \frac{\mu' f'_{21}}{\mu} \tag{13}$$

In Fig. **3** is plotted

$$E_D - E_0 = 0.088725\,[\sqrt{\mu} - \log f] \tag{14}$$

for four values of the ionization constant, including complete dissociation.[12] The fraction of the salt in the form of the primary ion at 0.1 M is approximately 8.0, 0.3, 0.7 and 0.8. For extremely dilute solutions the limiting law still holds, but the effect of association increases very rapidly, yet soon becomes nearly constant (curves nearly parallel) because of the rapid decrease in the activity coefficients. This leads to an inflection in very dilute solutions with a considerable range through which the curves are nearly rectilinear.

The curves of Fig. 3 have the same general shape as those of Fig. 2; by proper choice of ionic size and ionization constant they might be made to fit very closely. This hardly seems worth while, but the curves of Fig. **3** were used as guides in the extrapolation of those of Fig. 2 to zero concentration. The figure shows that, even with a theory which assumes the Debye–Hiickel limiting law at zero concentration, that law can be used as a guide only in extremely dilute solutions if there is a large amount of ion association. The assumption that the activity coefficient is the same as that of a typical strong electrolyte is even more dangerous, and the assumption that the logarithm of the activity coefficient is proportional to $\sqrt{c}$ and determination of the proportionality constant from the measurements themselves is still worse.

Discussion

These inflections at very low concentrations were first noted by Bjerrum.[13] They are discussed more specifically for a salt with high valence cation dissolved in one with high valence anion by LaMer and Mason,[14] and for ions of equal valences by Gronwall, LaMer and Sandved.[15] These authors attribute the inflections to the effect of higher terms in the power series expansion of the electrical density, which are neglected in the Debye–Hiickel treatment.

The computations which these latter authors have promised for unsymmetrical salt are not yet published. An examination of their Equations 34 and 64 for $\log f\pm$ shows that the ratio of the higher-order odd terms to the first, which is the Debye–Hiickel approximation, for a 2–1 salt with no foreign ions is from $^9/_{16}$ to $^4/_9$ the ratio for a 2–2 salt, and that the leading terms in the expansion of all the even terms, which are zero for a symmetrical salt, have the sign opposite to that of the odd terms, so that they tend to compensate. A closer examination of the first even term shows that it must remain positive to a considerable concentration.

Bjerrum's approximate method makes $\log f\pm$ for a 2–1 salt very nearly

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[12] The lowest value is nearly equal to that found for sulfuric acid (0.0115) by Sherrill and Noyes, THIS JOURNAL, ***48,*** 1861 (1926).

[13] Bjerrum, Kgl. *Danske Videnskab. Selskab, Math.-fys. Medd. VII, 9* (1926).

[14] LaMer and Mason, THIS JOURNAL, ***49,*** 410 (1927).

[15] Gronwall, LaMer and Sandved, *Physik.* Z., ***29, 358*** (1928).

the same as that for two ions with valence $\sqrt{2}$ at the same molal concentration, which is qualitatively consistent with the results of the other method. He treats the solutions as though they were incompletely dissociated with the constant for the *formation* of the binary compound depending on the size and valence in the following way

$$K' = 0.004\ \pi\ N\ (ab)^3 \int_2^b e^y y^{-4} dy$$

$$b = \frac{\epsilon^2\ z_1 z_2}{DkT}\frac{1}{a}$$

N is Avogadro's number, k the Boltzmann constant, ϵ the charge on the electron, D the dielectric constant, T the absolute temperature, z_1 and z_2 are the valences of the ions, and a is their effective mean diameter. The remainder of his computation differs only in details from that described in this article. The curves of Fig. 2 can be fitted approximately by attributing the sizes: $CdCl_2$ about 1.3 Å., $PbCl_2$ about 1.9 and $ZnCl_2$ from 3.5 to 6.

The properties of an electrolyte solution must depend on those of the solvent and of the individual ions, whether or not dissociation is complete. The original Debye–Hückel treatment, including the extensions to the higher terms cited above, considers only the dielectric constant of the solvent, and the valence and mean collision diameter of the ions. Hückel[16] has included the effect of the ions on the dielectric constant of the solutions, and the general equations of Gronwall, LaMer and Sandved include this effect for the higher terms. These treatments all consider the ions as having spherical symmetry.

There is no question but that a general treatment must consider two kinds of dissymmetry: first, that of the isolated ions, as illustrated by the nitrate and acetate ions; and second, that induced by an electrical field because of the deformability of the ion. The second effect is probably responsible for a large part of what Bronsted terms "specific interaction of ions" and in extreme cases for chemical association. Since it depends upon a very close approach of the ions, it may be expressed to a good approximation by the law of mass action.[17]

The effect of higher terms and that of deformability may each be approximated by assuming chemical combination, and the only difference is that the first makes the association constant a function of the size while the second makes it an independent parameter. Since the further effect of the size is of a smaller order, it would require great confidence in the accuracy of the experimental measurements and in the validity of the Debye method to differentiate between the two effects from measurements on a single salt.

[16] Hückel, *Physik. Z.*, 26, 93 (1925).

[17] The authors make no claim of originality for this treatment. It has been discussed more or less specifically in many places. See especially Fajans, *Trans. Faraday Soc.*, 23. 357 (1927).

The correlation of measurements on a large series of salts, when they are available, may give interesting information.

We can say with assurance that for higher valence ions part, at least, of the association constants must be attributed to the higher terms. This effect seems sufficient for the rare gas type ions, though deviations might be expected with the larger anions and high valence cations, and for some polyatomic ions. The authors believe that, whenever the assumption of spherical symmetry leads to a value of a less than two Ångström units, some other explanation should be sought, and that deformation often plays an important part in other cases. Certainly, unless the values in Table II are considerably in error two, and probably three, specific parameters (which might be the size, deformability, and effect on the dielectric constant) are required to fit both barium chloride and zinc chloride. No theory assuming spherical non-deformable ions can account for the transference number of the cadmium ion becoming negative,[18] or for the behavior of a weak electrolyte like acetic acid. It should be noted that we have no definition of association precise enough to determine the extent of it exactly or even to recognize its existence in small quantities.

Results

For the cell ZnHg (2 phase), $ZnCl_2$, AgCl, Ag we obtain $E_0 = 0.9834$ v. Combining this with Cohen's[19] value of 0.0006 v. for the difference in potential between zinc and the two-phase amalgam, and —0.2224 v. for the silver chloride electrode,[20] we obtain

$$\text{Zn, ZnCl}_2\text{, AgCl} \quad E_0 = 0.9840 \text{ v.}$$
$$\text{Zn, Zn}^{++} \quad E_0 = 0.7616 \text{ v.}$$

Lewis and Randall give the values 0.9839 and 0.7551. The close agreement of the first is somewhat of a coincidence; the difference in the second is due to the high value attributed to Horsch's silver chloride electrodes.

For the cell PbHg (2 phase), $PbCl_2$, AgCl, Ag we obtain $E_0 = 0.3430$ v. Carmody, extrapolating as a linear function of $\sqrt{m}$, obtained 0.3426.

For the cell Cd, $CdCl_2$, AgCl, Ag (Horsch) we obtain $E_0 = 0.5678$ v. Lewis and Randall give 0.5700 v.

In Table II are given values of the activity coefficient for several of the bivalent metal chlorides at rounded concentrations. The values for zinc, lead and cadmium chlorides are computed from the data discussed in this paper. The computations for calcium chloride are made from Equation 1 of the preceding paper[5] with the constants there given. For barium chloride a similar equation was used with $\alpha = 2.3$, $\beta = 0.0136$ volt, and $c/m = 0.99707 - 0.0286\,m - 0.00139\,m^2$.

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[18] See McBain and Van Rysselberge, THIS JOURNAL, 50, 3009 (1928).

[19] Cohen, *Z. physik. Chem.*, 34, 612 (1900).

[20] Scatchard, THIS JOURNAL, 47, 2098 (1925).

TABLE II

ACTIVITY COEFFICIENTS ($\gamma = a/m$) AT 25° OF CHLORIDES OF BIVALENT METALS

m	$CaCl_2$	$BaCl_2$	$ZnCl_2$	$PbCl_2$	$CdCl_2$
0.0001	0 961	0 961	0 960	0 958	0.923
0002	.947	.947	.945	939	.885
.0005	.918	918	.913	.902	.818
001	888	889	.881	859	.755
002	850	850	838	803	.684
005	785	.784	.767	704	.569
0 1	725	724	708	612	.475
02	658	655	.642	.497	.384
.05	.570	561	.556	..[a]	.277
1	515	494	502		.206
.2	481	438	448		.149
3	482	413	415		.121
.4	.496	400	393		104
.5	519	393	376		.093
.6	.548	.390	364		.083
.8	.622	391	343		.070
1.0	.715	.397	325		.061
1 25	.863	.409	.306		.054
1 5	1 047	.425	.290		048

[a] In a saturated solution, m = 0.03905, γ = 0.413.

Summary

The electromotive force of the cell $ZnHg_x$ (2 phase), $ZnCl_2$, $AgCl$, Ag has been measured at 25° from 0.003 to 1.5 M.

Measurements on barium chloride agree with the Debye–Hückel equation, assuming complete ionization. Those on zinc chloride, lead chloride and cadmium chloride do not, but they may be fitted by assuming incomplete dissociation of the primary ion. The effect of incomplete dissociation is calculated and values of the standard cell potentials and activity coefficients are computed. The relation of the apparent association to the "higher terms" and to the deformability of the ions is discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GREENSBORO COLLEGE]

TERNARY SYSTEMS: WATER, TERTIARY BUTANOL AND SALTS AT 30°

BY P. M. GINNINGS AND DOROTHY ROBBINS

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Tertiary butanol has been more or less a laboratory curiosity until recent years but economical methods of manufacture from the by-products of cracking petroleum have opened up a new field of potential uses. A résumé is given by Davis and Murray[1] concerning the chemical properties, solvent powers and physiological properties of the aliphatic tertiary alcohols and their industrial possibilities. Investigation of some of the physical properties of one of these, tertiary butanol, seems to have lagged behind that relative to the chemical properties. For example, while most of the aliphatic alcohols entirely miscible with water have been investigated as regards the two liquid phase formation in the familiar salting out phenomena when an aqueous solution of the alcohol is shaken with various salts, little has been done with tertiary butanol. Search of the literature revealed that the ternary systems water, tertiary butanol and salts had been investigated only partially in one paper,[2] in which potassium chloride was the only salt tried with the tertiary butanol. Investigation of this set of ternary systems seemed desirable for two reasons: first, tertiary butanol is the only aliphatic tertiary alcohol entirely miscible with water; second, it has the highest molecular weight of any simple aliphatic alcohol that is entirely miscible with water. The other butanols are only partially miscible with water.

While there are many inorganic salts that will cause the formation of two liquid phases in the above three-component system, only ten diversified salts were investigated in detail here. Some of these salts had been used in investigations of analogous systems; some were chosen in order to find the most effective salting-out agent; and the four potassium halides were selected primarily in order to compare their respective binodal curves. The system of graphical representation of the binodal and conjugation curves, interpolation to the plait point and phase composition used here is similar to that used in the "International Critical Tables," Vol. III, p. 398.

The aliphatic alcohols entirely miscible with water are methanol, ethanol, propanol, isopropanol, 1-propenol (allyl alcohol) and tertiary butanol. Fortunately, for the sake of comparison, all of the above alcohols have now been investigated as regards their behavior with aqueous

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[1] Davis and Murray, *Ind. Eng. Chem.*, 18, 844 (1926).

[2] Timmermans, *Z. physik. Chem.*, 58, 129 (1907).

potassium carbonate solutions. If the binodal curves of all are plotted upon the conventional triangular diagram and a perpendicular line is drawn from the alcohol–salt axis to the water apex, there will be a series of intersections between this line and the respective binodals in the following order: methanol, ethanol, isopropanol, 1-propenol, tertiary butanol and propanol. The tertiary butanol binodal lies very close to the propanol binodal. A little inspection here of the order reveals how unsaturation, branched carbon chain and progression in the homologous series affect the binodals in these ternary systems.

Sodium carbonate seems to have the highest specific salting-out effect because the binodal curve approaches nearest to the water apex. However, the ratio of the concentration of the alcohol to that of the water, in the salt-rich phase, is probably a better measure of the salting-out effectiveness; the smaller the ratio, the more effective the salt. In this respect, potassium carbonate and potassium fluoride in concentrated solutions surpass the sodium carbonate and seem to be the most effective of the ten salts investigated. This seems to be in agreement with the results from several investigations of salting-out agents.[3] In some cases, such as potassium iodide, the binodal curve terminates abruptly at both ends because the two liquid phase formation ceases. In other cases, such as potassium carbonate and potassium fluoride, the binodal curves approach the alcohol–water and water–salt axes with a very small slope. If a comparison is made of the four binodal curves of the potassium halides, the effectiveness seems to be an inverse function of the molecular weight of the potassium halide, potassium fluoride being the most effective.

Although determination of the binodal curves was the main object of this investigation, the conjugation curves were determined approximately, and also the intersection of the two, the plait point. The authors believe that the binodal curves here are in error by less than 1% in any case, and probably within 0.3% in many cases. However, the method used for the determination of the conjugation points allows a large possible error in some of the systems; this is especially true where the binodal curve follows quite closely and almost parallel to the alcohol–water axis. Here the $dC_{\text{alc.}}/dC_{\text{salt}}$ is very large, making the exact composition of the alcohol-rich phase as regards alcohol content difficult of determination by the indirect method used. Where the binodal curve is neither near nor almost parallel to the alcohol–water axis—as in the system with potassium iodide—the conjugation curve is relatively accurate. Usually, the sum of the weights of the three components in the mixture was from five to fifteen grams.

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[3] Frankforter and Frary, "Orig. Com. 8th Intern. Congr. **Appl.** Chem.," 22, 87–127; C. A., **7,** 44 (1913); Frankforter and Frary, J. Phys. Chem., **17,** 402–473 (1913); Frankforter and Cohen, THIS JOURNAL, 36, 1103–1134 (1914).

Experimental

The synthetical method was used throughout in the determination of the binodal curves. Known weights of each of the three components were introduced into a tapered centrifuge tube; the salt (c. p.) from a weighing tube weighed accurately to one centigram, the tertiary butanol (Eastman) and water from their respective burets. By careful and repeated trials with much shaking, the quantities of the three components in the tube were so regulated that the second liquid phase was at the point of appearance or disappearance. Observation of the cloudiness along with the use of the centrifuge to estimate the volume of the second liquid phase seemed to be the best method for the determination of the binodal points. The tube was shaken thoroughly in a well-stirred water-bath at 30° (plus or minus 0.2°) as the last step in the determination of each binodal point. The quantities of the three components were expressed as weight percentages, and so graphed on the triangular diagram.

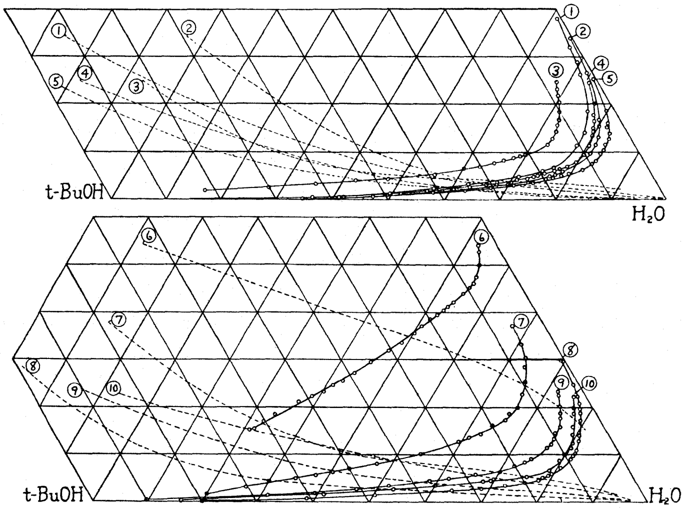

Fig. 1.—1, $(NH_4)_2SO_4$; 2, K_2CO_3; 3, NH_4Cl; 4, Na_2SO_4; 5, Na_2CO_3; 6, KI; 7, KBr; 8, KF; 9, KCl; 10, NaCl; ——, binodal; - - - - - -, conjugation.

An indirect analytical method was used for the determination of the conjugation points; indirect in the case of the alcohol-rich layer and direct in the case of the salt-rich layer. Two liquid phases were set up in equilibrium in the tube and brought to the correct temperature of 30° in the water-bath. Then a rubber stopper, perforated with two glass tubes, was inserted into the centrifuge tube, thereby producing a miniature wash bottle. By obtaining the difference between weighings (plus or minus 1 cg.), known weights of the two liquid phases were withdrawn into two weighed crucibles. Evaporation to dryness of the pair of crucibles corresponding to the two liquid phases and weighing gave the salt content of both phases. But according to the custom of preparation of the conjugation curves in the "International Critical Tables," the salt content of the salt-rich phase is plotted against the alcohol content of the alcohol-rich phase, so the alcohol content of the alcohol-rich phase was determined by notation of the salt content, reference to the binodal curve and intrapolation or extrapolation to the point required. Similarly, the segment of the conjugation curve on the opposite side of the binodal curve was obtained by plotting the alcohol content of the salt-rich phase against the salt content of the alcohol-rich phase. The intersection of the line uniting the two segments, just mentioned, with the binodal curve gave the plait point.

TABLE I

EXPERIMENTAL RESULTS

T-BuOH, wt. %	KI, wt. %	T-BuOH, wt. %	KF, wt. %	T-BuOH, wt. %	NH_4Cl, wt. %	T-BuOH, wt. %	Na_2SO_4, wt. %	T-BuOH, wt. %	Na_2CO_3, wt. %
62.8	15.5	60.6	0.8	82.0	2.0	58.6	0.3	52.3	0.7
60.3	16.9	48.3	1.4	70.2	2.4	47.0	1.2	50.0	1.0
57.7	18.5	34.1	2.3	61.2	3.3	42.2	1.6	41.3	1.3
52.0	20.9	28.6	2.8	54.1	3.7	37.2	2.2	35.4	1.8
49.2	22.1	24.1	3.3	47.9	4.2	33.7	2.6	30.8	2.1
46.5	23.4	20.4	3.7	39.3	5.0	31.1	2.9	26.2	2.8
44.3	24.6	17.7	4.5	33.4	6.4	28.8	3.4	22.4	3.3
42.0	25.5	16.6	5.1	30.2	6.6	26.3	3.6	19.7	4.0
39.2	27.0	15.4	5.6	27.5	7.4	24.9	3.9	18.1	4.6
35.1	29.5	14.9	5.7	25.3	8.0	22.9	4.2	16.6	5.0
30.6	31.9	12.5	7.0	23.2	8.6	21.5	4.6	15.3	5.4
27.6	33.4	9.7	8.8	22.0	9.0	20.8	4.9	11.9	6.0
24.2	35.6	8.7	9.6	20.7	9.4	19.5	5.3	9.9	7.2
22.1	37.0	8.2	10.0	19.8	10.0	17.5	5.8	8.6	8.0
19.9	38.6	7.7	10.9	15.7	11.5	16.4	6.2	6.8	9.7
17.9	39.6	6.3	12.7	14.1	12.7	14.3	6.9	6.1	10.4
16.6	40.3	5.6	14.0	12.9	14.3	12.4	7.8	5.2	11.2
15.4	41.1	3.8	16.9	11.8	15.6	10.2	9.5	4.0	12.9
13.9	42.3	2.8	18.7	11.0	16.8	8.1	11.4	3.3	14.1
11.3	44.0	2.4	19.7	10.2	18.4	6.7	13.3	3.1	15.3
9.6	45.4	1.9	20.7	9.2	20.3	6.1	14.2	2.5	16.0
8.4	46.1	1.6	22.2	8.7	21.7	5.5	15.2	1.5	18.9
7.2	47.3	1.2	24.6	8.1	23.2	4.8	16.5	0.6	25.2
5.2	49.8	0.7	29.8	7.6	24.7	3.9	17.9		
4.0	52.9	0.2	51.9			3.0	19.8		
3.3	54.7					1.8	24.5		

T-BuOH, wt. %	KCl, wt. %	T-BuOH, wt. %	KBr, wt. %	T-BuOH, Wt. %	NaCl, wt. %	T-BuOH, wt. %	$(NH_4)_2SO_4$, wt. %	T-BuOH, wt. %	K_2SO_3, wt. %
67.3	1.4	70.2	3.1	83.8	0.3	63.4	0.4	57.5	0.7
58.4	2.0	65.7	4.2	57.3	1.5	48.8	1.4	39.3	1.8
50.9	2.6	60.7	4.8	44.4	2.4	40.7	2.4	26.9	3.1
43.8	3.3	56.9	5.4	36.4	3.2	34.3	3.2	18.9	4.8
36.6	4.5	53.4	6.1	27.7	4.3	28.2	4.0	17.7	5.1
33.3	4.8	50.3	6.7	26.0	4.5	24.6	4.6	16.1	5.8
28.3	5.6	44.7	7.8	19.4	5.1	19.8	5.7	12.8	7.2
23.9	6.2	35.7	10.0	14.5	6.7	17.4	6.5	9.1	9.8
20.5	7.4	29.7	11.9	11.5	9.0	8.9	13.0	7.5	11.4
18.2	8.1	27.7	12.6	10.0	10.0	7.7	14.1	5.9	13.3
16.5	9.0	25.6	13.4	8.5	11.2	5.3	18.2	4.5	15.4
12.5	11.4	22.8	14.3	7.5	12.5	2.5	26.1	3.5	17.0
11.5	12.2	20.0	15.7	6.7	14.1	1.8	28.7	0.9	26.7
10.5	13.3	17.0	17.0	5.8	15.6	1.4	32.1	0.4	34.2
9.4	14.6	13.4	19.8	5.6	15.7	0.8	37.8		
7.9	15.9	11.3	22.6	4.2	18.4				

TABLE I *(Concluded)*

T-BuOH, wt. %	KCl, wt. %	T-BuOH, wt. %	KBr, wt. %	T-BuOH, wt. %	NaCl wt. %
7 0	176	9 2	253	3 6	198
6 4	18.6	7 7	285	2 7	224
5 9	200	6 8	304		
4 8	226	6 1	331		
4 5	233				

TABLE II

CONJUGATION DATA

(A) Tertiary butanol in the tertiary butanol-rich phase, weight per cent. (B) Salt in the salt-rich phase, weight per cent. (P. P.) Plait point.

(A)	(B)	(A)	(B)
99	29 8 KF	82	24 7 NH_4Cl
64	4.3 KF	80	22 7 NH_4Cl
60	4 1 KF	65	10 1 NH_4Cl
55	3.4 KF	44	5 0 NH_4Cl P. P.
36	2 2 KF P. P.	99	37 8 $(NH_4)_2SO_4$
90	23 3 KC1	82	27 4 $(NH_4)_2SO_4$
57	7 1 KCl	60	12 1 $(NH_4)_2SO_4$
53	6 7 KC1	42	5.1 $(NH_4)_2SO_4$
39	4 2 KCl P. P.	32	3 7 $(NH_4)_2SO_4$ P. P.
78	37 0 KBr	93	24 5 Na_2SO_4
76	34 2 KBr	68	11 5 Na_2SO_4
64	19 1 KBr	66	10 5 Na_2SO_4
42	8 7 KBr P. P.	50	4 6 Na_2SO_4
63	54 7 KI	37	2 5 Na_2SO_4 P. P.
50	47 1 KI	69	34 2 K_2CO_3
45	45 5 KI	62	24 4 K_2CO_3
26	34 6 KI P. P.	53	14 8 K_2CO_3
84	22 4 NaCl	27	3 2 K_2CO_3 P. P.
60	13 9 NaCl	97	25 2 Na_2CO_3
48	10 7 NaCl	70	7 7 Na_2CO_3
23	4 6 NaCl P. P.	55	4 5 Na_2CO_3
		35	2 0 Na_2CO_3 P. P.

Summary

1. Tabular data, binodal curves, conjugation curves and plait points are given for the ternary systems of tertiary butanol and water with ten inorganic salts.

2. A comparison is made between the binodal curves of the systems water, alcohol and potassium carbonate, when the alcohol varies among the water-miscible aliphatic alcohols.

3. Potassium carbonate and potassium fluoride are the most effective salting-out agents of the ten salts investigated.

4. The value of the respective potassium halides as salting-out agents seems to be an inverse function of the molecular weight of the halide, potassium fluoride being the most effective of the four.

GREENSBORO. NORTH CAROLINA

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE DROP WEIGHT METHOD FOR THE DETERMINATION OF SURFACE TENSION. THE EFFECT OF AN INCLINATION OF THE TIP UPON THE DROP WEIGHT

BY DAVID M. GANS AND WILLIAM D. HARKINS

RECEIVED FEBRUARY 10, 1930 PUBLISHED JUNE 6, 1930

Introduction

The drop weight method has been developed as an accurate method for the determination of surface tension. If the greatest accuracy is not required, a simple form of apparatus gives reliable measurements with ease and rapidity. For any type of work, the variation of the drop weight with the angle of inclination of the tip should be known, and so the requisite values were determined.

Results

With the apparatus and procedure described in detail elsewhere,[1] the drop weights for conductivity water were determined at 25.0°, with the tip at various angles of inclination. The angle a which the tip made with the horizontal plane was set at from 0.0 to 20.0°, and was measured to within 0.1° by the use of a level. At an angle of 3.0°, the inclination of the tip was very apparent to the eye.

Table I gives the average weights in air of one drop of water. The apparent surface tension, for an observer unaware of the tilt of the tip, may be calculated by means of the equation

$$\gamma = \frac{Mg}{2\pi r}\,\phi\left(\frac{r^3}{v}\right) \qquad (1)$$

in which M is the weight of the drop in air, g is the acceleration due to gravity, r is the radius of the tip (0.2989 cm. in the present case) and ϕ, a function of r^3/v where a is the volume of the drop, is the empirical correction factor of Harkins and Brown,[1] taken from a graph of their results. These calculated surface tensions were plotted against the corresponding angle α, and from the smoothed curve, which passed exactly through four of the points and came within 0.07 dyne of the other two, the apparent surface tention γ_α was read for each value of a employed. Since γ_α is the apparent surface tension when the dropping surface makes the angle $a!$ with the horizontal, γ_0 will be the surface tension when the dropping surface of the tip is accurately horizontal, that is, the true surface tension of water at this temperature. In Col. 3 of Table I are given the differences $\gamma_0 - \gamma_\alpha$. The apparent surface tension is obviously not very different from the true value, when a is less than 5.0°. When α is 20.0°, which is a very large

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[1] I-Tarkins and Brown, THIS JOURNAL, 41, 499 (1919).

angle under the conditions, this difference is only 2.3% of γ_0 for the tip used.

TABLE I

AVERAGE WEIGHTS IN AIR OF ONE DROP OF WATER

α	M	$\gamma_0 - \gamma_\alpha$	$\gamma_0 - \gamma'$	$2.025 \times 10^{-4}\alpha^3$
0.0°	0.08424	0.00	0.00	0.00
6.0°	.08420	.03	− .08	.03
7.5°	.08420	.10	− .20	.09
10.0°	.08391	.23	− .18	.20
15.0°	.08333	.73	− .26	.68
20.0°	.08224	1.62	− .16	1.62

It is desirable to know, first, whether the true surface tension of water may be calculated from a measurement of the drop weight at a large angle α, and, second, how large α may be without affecting the results appreciably.

When the tip is inclined, its projection upon a horizontal plane is no longer a circle of radius r, but an ellipse of semi-major axis r and semi-minor axis r cos α. Therefore, the drop weight should not be that for a circular tip of radius r, but would more nearly correspond to that for a circular tip of radius r', where r' would be an average semi-axis of the ellipse. The surface tension should be given more accurately by

$$\gamma' = \frac{Mg}{2\pi r'}\,\phi\left(\frac{r'^3}{v}\right) \qquad (2)$$

provided the proper value of r' is known.

If the radius of the circle whose circumference is that of the ellipse is taken for r', then $r' = r\sqrt{(1 + \cos^2\alpha)/2}$ very nearly. The calculated values of $\gamma_0 - \gamma'$ are given in Col. 4 of Table I. For all values of α, Equation 2 gives results that are within 0.4% of the true surface tension. For small values of α, however, the results obtained with Equation 1 are better. If r' is taken to be the radius of the circle whose area is that of the ellipse, then $r' = r\sqrt{\cos\alpha}$. The results in this case are practically identical with those already listed in Col. 4 of Table I. Other methods for obtaining the average r' may lead to smaller values of $\gamma_0 - \gamma'$. Equation 2 thus gives a good approximation for the true surface tension.

To determine what the values of γ_α are for small angles α, equations of various forms were fitted to the data in Col. 3 of Table I. The equation

$$\gamma_0 - \gamma_\alpha = 2.025 \times 10^{-4}\alpha^3 \qquad (3)$$

for α in degrees was found to fit well, as is shown in Col. 5 of Table I. By means of this equation, the values of $\gamma_0 - \gamma_\alpha$ for the small angles in Table II are secured. The values of γ_α are also included, for 71.97 dynes per cm. as the accepted surface tension[2] of water at 25.0°. For angles of inclina-

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[2] "International Critical Tables," McGraw-Hill Book Co., New York, Vol. IV, p. 447.

TABLE II

VALUES FOR SMALL ANGLES

α	$2.025 \times 10^{-4}\alpha^3$	γ_α	α	$2.025 \times 10^{-4}\alpha^3$	γ_α
0.00°	0.000	71.97_0	4.00°	0.013	71.95_7
0.25°	.000	71.97_0	5.00°	.025	71.94_5
0.50°	.000	71.97_0	6.00°	.044	71.92_6
1.00°	.000	71.97_0	8.00°	.104	71.86_6
2.00°	.002	71.96_8	10.00°	.203	71.76_7
3.00°	.005	71.96_5			

tion less than 3°, the effect of the tilt on the calculated surface tension is not appreciable. Unlike other methods for the determination of surface tension, the drop weight method is thus particularly insensitive to any inclination of the measuring apparatus. The utmost precautions need not therefore be taken to insure a horizontal dropping surface, and a setting of within 2° of the horizontal, an angle quite apparent to a trained eye, will probably suffice in all cases.

Summary

Results obtained with the drop weight method for the determination of surface tension are found to be unaffected by a slight inclination of the apparatus. The effect upon the weight of a drop of a tilt of the tip of less than 3° is not appreciable. Precautions need not, therefore, be taken to set the dropping surface at an angle of less than 2° with the horizontal.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE SURFACE TENSION OF AQUEOUS SOLUTIONS OF PARA-TOLUIDINE

BY DAVID M. GANS AND WILLIAM D. HARKINS

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1. Introduction

During the progress of work in this Laboratory on surface phenomena, there arose a need for reliable data on the surface tension of aqueous solutions of *p*-toluidine. Such measurements had already been made by Edwards,[1] who used a modification devised by Ferguson of the capillary height method, and by Frumkin, Donde and Kulvarskaya,[2] who employed the capillary height method. The two sets of results are in very poor agreement. While Frumkin did not lay claim to great accuracy in his own determination,[3] these showed the work of Edwards to be seriously in error.

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[1] Edwards, *J. Chem. Soc.*, 127, 744 (1925).

[2] Frumkin, Donde and Kulvarskaya, *Z. physik. Chem.*, 123, 321 (1926).

[3] Private communication.

2. Method, Apparatus, and Procedure

For the measurement of the surface tension of aqueous solutions of *p*-toluidine and similar substances, the drop weight method has certain advantages. For while such solutions wet with ease the ground-glass tip used in the drop weight method, it has been observed that solutions of even very pure *p*-toluidine wet polished glass with some difficulty. The capillary height method is therefore not suitable.

The apparatus which was employed is shown in Fig. 1, and is a modified form of the standard apparatus described by Harkins and Brown.[4] The metal box B, which contains the glass tip, adequately cleaned, and the solution, is immersed in a thermostat kept accurately at 20.0°. The ground surface of the glass tip is maintained in the horizontal plane indicated by the L-shaped level shown. Each drop is pulled over to almost full size by very gentle suction at a rubber tube attached to the metal tip-holder A. The first drop is allowed to hang for some minutes in the weighing bottle V, in order to saturate the enclosed air with the vapors from the solution. The drop is then drawn over and made as large as is possible without causing it to fall, and the level between the bottles S and V is so adjusted that the drop falls as slowly as is possible. The supply bottle S is raised or lowered for this purpose by means of the microscope stand T. This adjustment is accomplished through the pinion head P which is attached to the microscope stand by means of a small universal joint and a long metal rod that extends to the chair of the operator, who watches the formation of the drops through a small telescope, the cross hairs of which mark the maximum size of the stable drop and thus help in its control. When the required number of drops has been drawn over, the metal box is at once removed from the thermostat and opened, the weighing bottle V is chilled for exactly one minute in an ice-water mixture in order to condense most of the vapors within, and the bottle is removed, quickly stoppered and weighed.

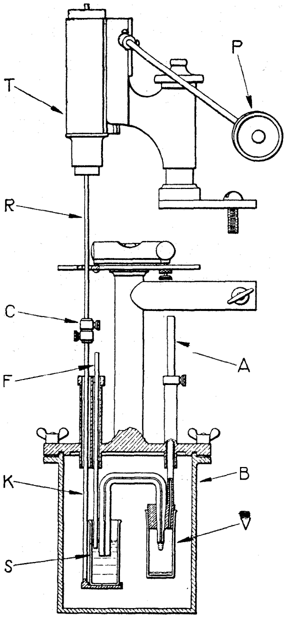

Fig. 1.—Apparatus for the accurate determination of surface tension by the drop weight method.

3. Results

In the work here reported, each determination consisted of one run of twenty drops, and another, immediately following, of five drops. The

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[4] Harkins and Brown, THIS JOURNAL, 41, 499 (1919).

difference represented the weight, in their own saturated vapor, of fifteen drops. In this difference the errors caused by the weight of the moisture condensed on the interior of the bottle by chilling are mostly eliminated. Three such determinations were made with each solution, and the average per drop was taken as the drop weight for that solution. Of the three results, none differed from the average by as much as 0.15%, while in only two of the twenty-seven single determinations was this difference greater than 0.10%.

The drops were usually allowed to hang for twenty to thirty seconds before they were permitted to fall. That this length of time was sufficient to enable the surface of the drop to attain equilibrium with the interior of the drop was demonstrated by work with a solution, containing 0.00606 mole of p-toluidine per kilogram of water, which, since this was the most dilute solution studied, gave the slowest diffusion into the surface. The drop weight was determined for drops which maintained approximately their full size, before falling, for four minutes, and also for about twenty seconds each. The two results differed from their mean by only 0.08%. Apparently an age of one-half minute for the full-sized drop gives equilibrium of the surface with the liquid and the vapor phase.

With the solution containing 0.03376 mole of p-toluidine per kilogram of water, the drop weight of drops held at almost full size for four minutes differed from that of drops held at full size for twenty-five seconds each by only 0.06%. This demonstrates that, even for this relatively concentrated solution, oxidation of the *p*-toluidine in the surface of the drop did not take place to a sufficient extent to alter the surface tension of the solution.

The density of each solution at 20.0° was determined in duplicate with a pycnometer of approximately 20-cc. capacity, the volume of which was accurately determined with conductivity water as the standard.

Experiments were carried out over practically the entire concentration range. The results are given in Table I. In Col. 5 is listed the weight of a single drop in air saturated with the vapor from the respective solution.

TABLE I

SURFACE TENSION OF AQUEOUS SOLUTIONS OF *p*-TOLUIDINE

Soln.	Mole per kg. of water, m	Mole per kg. of soln.	Log, m	Density, g. per cc. at 20.0°	Drop weight, g.	Volume per drop, V, in cc.	r^3/v		γ in dynes per cm. at 20.0"
1	0.00000	0.00000	— w	0.99820	0.085367	0 08562	0 3119	1.6327	72.75
2	.00606	.00606	−5.1069	,99830	,083970	.08421	.3172	1.6343	71.63
3	.00716	.00715	−4.9402	,99832	,083658	,08390	.3184	1.6347	71.38
4	.01174	.01172	−4.4455	.99832	.081734	.08197	.3258	1.6367	69.82
5	.01985	.01981	−3.9202	.99837	,075256	,07547	.3539	1.6440	64.57
6	.02753	.02745	−3.5931	,99834	.070120	,07032	.3798	1.6499	60.38
7	,03376	.03364	−3.3891	.99828	,066889	.06708	.3982	1.6537	57.73
8	.04935	.04909	−3.0093	,99838	.060395	,06057	.4410	1.6606	52.35
9	.06218	.06177	−2.7781	.99843	.056533	.05669	.4712	1.6641	49.10

Each value is the average of three determinations, as outlined above. In Col. 7 is given the calculated value of r^3/v where r, the radius of the tip used, is 0.29892 cm., the average of measurements made with a calibrated traveling microscope over six different diameters, and v is the volume of the drop in question. The experimentally determined correction factor Φ tabulated in Col. 8 is a function of r^3/v and was taken from a graph which plots the values of Harkins and Brown.

The equation by means of which the surface tension was calculated is

$$\gamma = \frac{Mg}{2r}\Phi$$

in which γ is the surface tension in dynes per centimeter, M is the weight in grams of the drop in air saturated with the vapors from the solution, g is the acceleration due to gravity, which is 980.28 cm. per sec. per sec. in this Laboratory, and r and Φ have the significance pointed out above.

4. Purification of Materials

The p-toluidine used was obtained from the Eastman Kodak Company and was purified from it isomers and other impurities as recommended, in general, by Berliner and May.[5] The p-toluidine was twice distilled, the end fraction being discarded each time. It was dissolved in five times its volume of ether, and the oxalate precipitated by addition of an ethereal solution of oxalic acid. The salt was washed with ether and recrystallized four times from hot water. A little oxalic acid was added to the water each time to hinder hydrolysis. The p-toluidine was liberated with sodium carbonate solution, recrystallized from hot water, steam distilled and again recrystallized from hot water. The snow-white crystals were dried in *vacuo* over stick potassium hydroxide for twelve days. The elaborate purification reduced the yield to 15%. The crystals melted at 43.6°, while the value given by the "International Critical Tables" is 43.7".

Conductivity water was used for all of the solutions, which were made up by weight.

5. Comparison with Other Data

The measurements of Edwards were obtained at temperatures between 15 and 17.5°. The values which he found for the surface tension of water are higher than the corresponding value given by the "International Critical Tables."[6] His values were, therefore, multiplied by 0.9780, which brings his average value for pure water to 73.34 dynes per centimeter, the accepted value. The densities at 20° of p-toluidine solutions are very nearly that of water, and so the densities at 16°, required for the conversion to the concentration units used in this paper, were obtained by adding to

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[5] Berliner and May, THIS JOURNAL, 49, **1007 (1927).**

[6] "International Critical Tables," McGraw-Hill Book **Co.,** New **York, Vol. IV, p. 447.**

the density of water at 16° the difference between the densities of the corresponding solution and of water at 20°.

The data of Frumkin, Donde and Kulvarskaya were corrected in the same way, by use of the factor 1.0022.

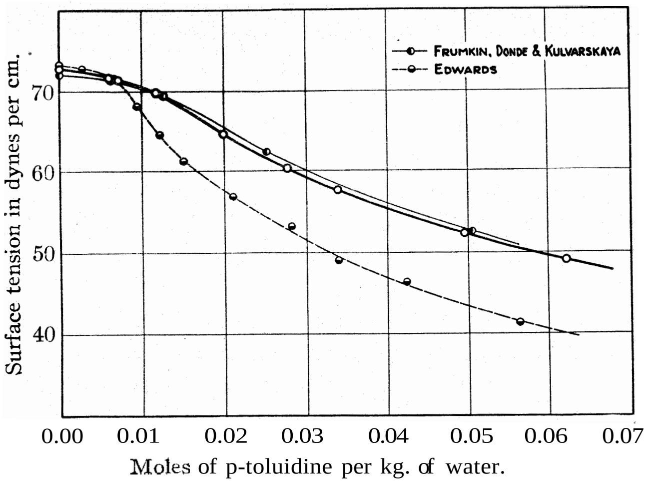

Fig. 2.—Surface tension of aqueous solutions of p-toluidine as given by different observers.

These data, together with those obtained in the present work, are given in Fig. 2. It is obvious that the results of Edwards are much too low. This difference is strikingly brought out in the logarithmic plot in Fig. 3;

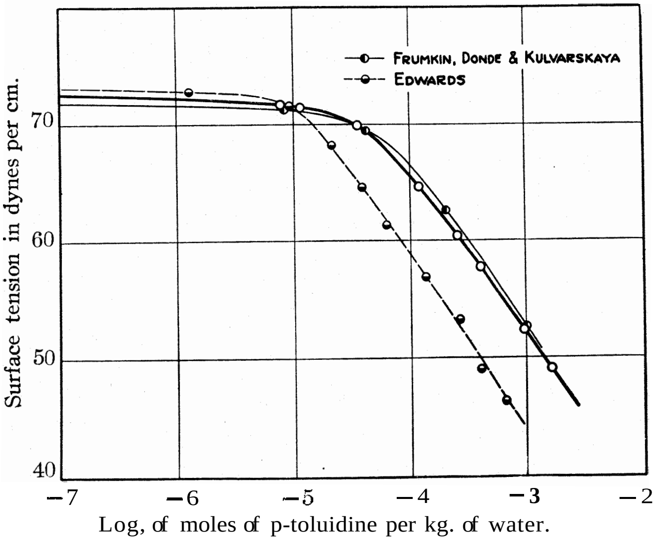

Fig. 3.—Surface tension of aqueous solutions of p-toluidine as given by different observers.

curiously enough, however, all of the three curves have almost the same slope in the straight portions of this graph.

6. Calculation of the Adsorption

The adsorption of p-toluidine at the air–solution interface may be calculated by means of the Gibbs adsorption equation

$$u = \frac{-1}{RT}\frac{d\gamma}{d \log_e a}$$

where γ is the surface tension in dynes per centimeter, a is the activity of the solute, R is the gas constant, **8.315** $\times 10^7$ ergs per mole degree, T is the absolute temperature and u is the number of moles of solute which must be added to the solution after the surface has been increased by one square centimeter, in order to bring the solution back to its initial concentration.

McBain and his co-workers[7] have found the activity of aqueous solutions of *p*-toluidine to be proportional to the concentration. While this result is probably not exact and is unexpected for a substance of the type of *p*-toluidine, the adsorption may, for the present, be calculated on this basis. In this case

$$d \log_e a = d \log_e m$$

in which m is the number of moles of solute per kilogram of water. The slope of the curve representing our data in Fig. **3** is, therefore, directly d γ/d $\log_e$ a.

The calculations are tabulated in Table II for the more concentrated solutions included in Table I. The adsorption is listed in Col. **3** as the number of moles per square centimeter of surface, in Col. 4 as the number of molecules per square centimeter of surface and in Col. **5** as the apparent surface area in sq. Å. occupied by each molecule.

TABLE II

ADSORPTION OF *p*-TOLUIDINE IN AQUEOUS SOLUTION CALCULATED BY THE GIBBS ADSORPTION EQUATION

Soln.	Mole per kg. of water, m	$\frac{-d\gamma}{d \log_e m}$	$u \times 10^{10}$	$u' \times 10^{-14}$	Area per molecule in sq. Å.	Mole per cc. of soln.	Mole per cc. of soln. $\times 10^{-21}$	Molecules, per sq. cm. of soln. $\times 10^{-14}$	Total no. of molecules. per sq. cm. $\times 10^{-14}$	Effective area per molecule, Sq. Å.
5	0.01985	12.14	4.981	3.02	33.1	0.04198	0.0120	0.05	3.07	32.6
6	.02753	13.25	5.436	3.30	30.3	.04274	.0166	.07	3.36	29.8
7	.03376	13.77	5.649	3.43	29.2	.04336	.0204	.07	3.50	28.6
8	.04935	14.10	5.785	3.51	28.5	.04490	.0297	.09	3.60	27.8
9	.06218	14.10	5.785	3.51	28.5	.04617	.0374	.11	3.62	27.6

If one square centimeter of new surface were to be instantaneously formed, a certain amount of solute would already be present in the fresh surface.

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[7] McBain, Wynne-Jones and Pollard, "Colloid Symposium Monograph," The Chemical Catalog Company, New York, 1928, Vol. VI, p. 57.

This amount is further increased by the quantity u which is then adsorbed. The total number of molecules in each square centimeter of surface is thus the sum of these two amounts. The number already in the surface is unknown, but may be taken as approximately the two-thirds power of the number of molecules in each cubic centimeter of solution, a value given in Col. 8. This correction is not great for solutions as dilute as these, but is considerable for more soluble substances. In Col. 10 is listed the corrected apparent area in sq. Å. occupied by each molecule in the surface region.

The apparent surface area per molecule of *p*-toluidine appears to be 28 sq. Å. The work of Adam[8] with insoluble films gives the value 23.8 sq. Å. for the benzene ring perpendicular to the surface. In view of the fact that the activity of solutions of *p*-toluidine is not known accurately, this agreement is satisfactory and serves as an indication that the adsorbed solute forms a monomolecular film on the surface of the solution.

7. Summary

1. The drop weight method for the measurement of surface tension has the advantage over the capillary height method in that the former is independent of the angle of contact, and can thus be used with substances like *p*-toluidine, whose aqueous solutions do not wet glass easily.
2. A slightly improved procedure for the determination of surface tension by the drop weight method is presented.
3. Measurements of the surface tension of aqueous solutions of *p*-toluidine by means of the drop weight method are given and compared with earlier results. *p*-Toluidine is a very surface-active substance, for at 20.0° it lowers the surface tension by 8.18 dynes when dissolved in water to the extent of 0.0199 mole per kilogram of solvent, and by 23.65 dynes with 0.0622 mole.
4. By use of the Gibbs adsorption equation, the area occupied by each molecule of *p*-toluidine in the surface region is found to be 28 sq. Å. for the nearly saturated solution, which is in agreement with the area expected from other sources for a monomolecular film.

CHICAGO, ILLINOIS

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[8] Adam, *Proc. Roy. Soc.* (London), **103,** 676 (1923).

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COOPERATION WITH THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITIES OF ARSENIC, ARSENIC TRIOXIDE AND ARSENIC PENTOXIDE AT LOW TEMPERATURES[1]

BY C. TRAVIS ANDERSON[2]

RECEIVED FEBRUARY 11, 1930 PUBLISHED JUNE 6, 1930

In continuation of its general program of determination of the heat capacities of the various metals and oxides which are important in metallurgical processes, the Pacific Experiment Station of the U. S. Bureau of Mines has studied the metals and oxides of arsenic, antimony and bismuth at low temperatures. The thermodynamic properties of the metals and oxides of this group are of practical importance because they constitute some of the lead smelters' most difficult problems of reduction and refining, and they also have considerable theoretical interest. The present article deals only with the heat capacities of arsenic and its oxides; later papers will discuss the remaining materials in this group.

Method and Apparatus

With the exception of a few minor details, the methods and apparatus used in this work are identical with those previously described from this laboratory by Millar.[3] The apparatus was provided with a new thermocouple, which was made of wire from the same spool as Thermocouple No. 17 of Giauque, Buffington and Schulze,[4] and which was compared with No. 17 through a secondary standard at the temperature of liquid air, the melting point of toluene crystals and the melting point of ice. The secondary standard was calibrated directly against No. 17 at 28 points by Kelley.[5]

The standard cell was calibrated from time to time against another having a Bureau of Standards certificate.

Using the graphical method of Giauque and Wiebe,[6] a new temperature scale was determined for the resistance thermometer, and it is probably somewhat better than the one previously used in this Laboratory.

The volt-box correction was redetermined by substituting a standard 100-ohm resistance for the calorimeter resistance. The volt-box factor was calculated from accurate measurements of current and voltage when small amounts of electrical energy were passed through the volt-box and standard

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Assistant Physical Chemist, Pacific Experiment Station, U. S. Bureau of Mines, Berkeley, California.

[3] Millar, THIS JOURNAL, 50, 1876 (1928).

[4] Giauque, Buffington and Schulze, *ibid.*, 49, 2343 (1927).

[5] Kelley, ibid., 51, 180 (1929).

[6] Giauque and Wiebe, ibid., 50, 101 (1928).

resistance. This value is probably more reliable than that previously obtained directly by measuring the high resistance which the volt-box contains.

The heat capacity of the empty calorimeter was redetermined, using the new temperature scale.

By the use of liquid nitrogen instead of liquid oxygen it was possible to cool down to about 55°K. with the present pumping facilities. This temperature is about 5° lower than that previously reached in this Laboratory.

Materials

The sample of arsenic used contained **0.13%** antimony, no lead or silica and more than 99.8% arsenic. Its density was found to be **5.48.** A **342.9-g.** sample was studied.

The arsenic trioxide was of C. P. grade, but was resublimed. Each particle was definitely crystalline and of octahedral structure. It analyzed better than **99.8%** arsenic trioxide and had a density of **3.85.** The calorimeter was filled with a **267.4-g.** sample.

The arsenic pentoxide was a very pure material which was dried at 550° after treatment with concentrated nitric acid. It contained more than 99.7% arsenic pentoxide. The only detectable contamination was **0.2%** arsenic trioxide. It contained no antimony. The material did not consist of separate crystals, as did the arsenic trioxide, but of crystalline aggregates; **179.7** g. of the pentoxide was used. It had a density of **4.32.**

Screen tests were made on these materials and the results are shown in Table I.

TABLE I

SCREEN SIZES OF SAMPLES MEASURED

Screen size	As, %	As_2O_3	As_2O_5
+ 35	0.25	...	80.6
+ 48	..	4.5	18.0
+ 65	35.0	2.0	..
+100	30 0	2.5	0.7
+150	13.5	2.5	..
+200	20.0	8.0	0 7
−200	1.25	80.5	..

The Specific Heats

The heat capacities of these substances expressed in gram calories (15°) per gram formula weight are given in Table II and are shown graphically in Fig. 1. In changing joules to calories the factor[7] 1/4.184 was used. The calculations were made on the basis of O = 16 and As = 74.96.

Calculation of Entropies.—The entropy calculations were made in the usual manner. The experimental heat capacity curves were extended below the lowest measurements, so as to approach and finally coincide with Debye functions having the following parameters (Θ): for As, 275; As_2O_3,

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[7] "International Critical Tables," Vol. I, p. 24.

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT

As		As_2O_3		As_2O_5	
T, °K.	C_p	*T*, °K.	C_p	*T*, °K.	C_p
57.2	2.400	60.2	5.839	63.5	4.511
61.1	2.458	63.9	6.200	67.1	4.947
70.2	2.889	76.9	7.646	80.8	7.101
80.9	3.584	89.0	8.647	91.6	8.266
85.2	3.536	100.0	9.702	101.9	9.713
91.0	3.703	108.1	10.55	114.0	11.57
98.6	3.883	121.1	11.98	127.8	13.31
115.5	4.481	132.0	12.95	143.5	15.10
128.2	4.626	143.0	13.80	160.9	17.01
140.6	4.800	154.9	14.90	173.2	18.41
155.5	4.990	168.9	16.14	184.1	19.29
174.4	5.137	181.0	16.92	168.5	17.91
202.7	5.448	194.7	17.93	181.5	19.28
212.7	5.536	210.4	19.00	196.9	20.70
227.1	5.592	223.0	19.58	209.8	21.89
242.4	5.743	241.9	20.48	222.0	22.87
258.9	5.767	253.7	21.23	239.1	24.10
267.2	5.734	272.2	21.83	251.1	25.08
272.8	5.754	288.7	22.46	270.3	26.50
285.7	5.848	291.6	22.61	287.1	27.45
291.0	5.900	296.6	22.78	291.7	27.69
				296.2	27.68

141; As_2O_5, 240. In Table III are given the results of the entropy calculations.

TABLE III

ENTROPIES FROM EXPERIMENTAL DATA

	As		As_2O_3	
Extrap.	(0-56.2)°K.	1.20	(0–56.2)°K.	3.54
Graph.	(56.2–298.1)	7.16	(56.2–298.1)	22.04
S_{298}		8.4 ± 0.2 E. U.		25.6 ± 0.4 E. U.

	As_2O_5	
Extrap	(0–63.1) °K.	1.94
Graph.	(63.1–298.1)	23.30
S_{298}		25.2 ± 0.4 E. U.

It was found possible to fit the molal specific heat curves of the two oxides by the following combinations of Debye and Einstein functions

$$C_{As_2O_3} = D\left(\frac{141}{T}\right) + 2D\left(\frac{567}{T}\right) + 2D\left(\frac{1054}{T}\right)$$

$$C_{As_2O_5} = D\left(\frac{240}{T}\right) + 2E\left(\frac{368}{T}\right) + 2E\left(\frac{727}{T}\right) + 2D\left(\frac{1600}{T}\right)$$

The arsenic trioxide combination fits the experimental results up to 298°K., and that for arsenic pentoxide up to 125°K. Above 125°K. the experimental curve for arsenic pentoxide begins to rise above that of the function sum, probably due to $C_p - C_v$ becoming appreciable. Similarly, it may be that C_p and C_v for arsenic trioxide are very nearly equal up to 298°K.

As a means of demonstrating the average agreement between the experimental results and these combinations, the entropies at 298°K. were calculated, using these function sums. The results obtained are for arsenic trioxide 25.6 E. U., and for arsenic pentoxide 25.2 E. U., which are identical with the values previously given. In calculating the entropy of arsenic pentoxide by use of the functions, it was necessary to add an entropy difference of 0.17 unit, representing the difference between the experimental curve and the theoretical curve, in order to obtain the above values.

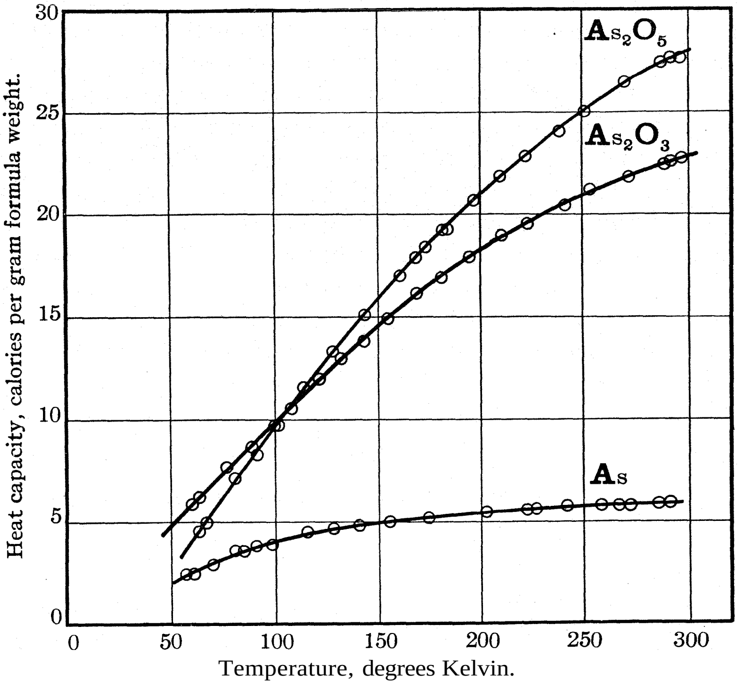

Fig. 1.—The heat capacities per gram formula weight of arsenic trioxide and arsenic pentoxide.

Related Thermal Data

The heats of formation of the oxides have been determined by Thomsen.[8] For arsenic trioxide he gives —154,700 Cal., and for arsenic pentoxide —219,400 Cal. Berthelot[9] gives —156,400 for the heat of formation of

[8] Thomsen, "Thermochemistry," Longmans, Greene and Co., London, 1908, p. *227.*

[9] Berthelot, "Thermochemie," Vol. II, 1897, p. 117.

arsenic trioxide. Schuhmann[10] determined the free energy of formation of arsenic trioxide from cell measurements. Correcting Schuhmann's result by the use of Eastman's[11] value for the free energy of formation of liquid water, ΔF°_{298} for arsenic trioxide was calculated to be $-137{,}000$ Cal. Using the integrated Gibbs–Helmholtz equation, Schuhmann calculated from the temperature coefficient of his cells, over a 20° temperature range, that the heat of formation of arsenic trioxide was $\Delta H_{298} = -153{,}800$. Previous experience at this Laboratory with oxide cells[12] has shown that free energies may be obtained from oxide cells with high precision, but because of the usually low magnitude of the cell coefficient, and the inherent fluctuations and polarizability of such cells, thermal values from this source are often not entirely satisfactory. It is justifiable, therefore, to calculate heats of formation from free energies and entropies, when these latter quantities have a high probable accuracy. In this way, using the free energy from Schuhmann's cell value, and the entropies of arsenic and arsenic trioxide, the heat of formation of arsenic trioxide was calculated as $-156{,}500$ Cal. This value agrees very well with the value of $-156{,}400$ given by Berthelot.

In the case of the pentoxide, direct free energy data are unavailable, and the free energy of formation of arsenic pentoxide was calculated from Thonisen's value of $-219{,}400$ Cal. for the heat of formation, and the entropies of arsenic and arsenic pentoxide, to be $\Delta F^{\circ}_{298} = -185{,}400$ Cal. All of the data are summarized in Table IV.

TABLE IV

SUMMARY OF ENTROPIES, FREE ENERGIES AND HEATS OF FORMATION

	S_{298}	ΔF°_{298}	ΔH°_{298}
As	8.4	....	....
As_2O_3	25.6	−137,100	−156,000
As_2O_5	25.2	−185,400	−219,400

In conclusion the author wishes to thank R. W. Millar for making the measurements on arsenic trioxide and arsenic pentoxide, and K. K. Kelley for his assistance in calibrating thermocouples, making the new temperature scale, and in fitting the Debye and Einstein curves to the experimental values.

Summary

The heat capacities of arsenic, arsenic trioxide and arsenic pentoxide from about 57 to 300° Kelvin have been determined, and the corresponding entropies calculated. The heat of formation of arsenic trioxide and the free energy of formation of arsenic pentoxide have been calculated.

BERKELEY, CALIFORNIA

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[10] Schuhmann, THIS JOURNAL, 46, **1445 (1924).**

[11] Eastman, Information Circular, Bureau of Mines, No. **6125,** p. **13,** May, **1929.**

[12] Maier, THIS JOURNAL, **51, 194 (1929).**

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COÖPERATION WITH THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITY OF SILICON AT LOW TEMPERATURES[1]

BY C. TRAVIS ANDERSON[2]

RECEIVED FEBRUARY 11, 1930 PUBLISHED JUNE 6, 1930

In continuation of its general program of determination of the heat capacities of the various metals and oxides which are important in metallurgical processes, the Pacific Experiment Station of the United States Bureau of Mines has studied an especially pure sample of metallic silicon.

The method and apparatus used in this work are identical with those described previously.[3]

The sample of silicon was furnished by the Electro Metallurgical Company of New York. According to their analysis, it had the following composition:

Si	99.20	C as Carbon	0.052
Fe	0 017	C as SiC	0.02
Al	0.009	Ni	Nil
Mn	Trace	Mg	Nil
Cu	Nil	O_2	0.17
Ca	<0. 01	N_2	0.009
Ti	Nil		
Cr	Nil		99.48%

The analytic determination of silicon in this grade of material is difficult, and since the probable impurities are well accounted for, the sample may actually be 99.7% pure, *i. e.*, 100% minus the known impurities. A 139.8-g. sample was studied.

Screen tests were made, and the results are shown in Table I. The density of the silicon used was 2.34.

TABLE I

SCREEN SIZES OF SILICON

Screen size	+65	+100	+150	+200	−200
Percentage	2.0	1 5	2.0	12.0	82.5

The Specific Heat

Measurements of the specific heat of silicon at low temperatures have previously been limited to six determinations of true specific heat by Nernst

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Assistant Physical Chemist, Pacific Experiment Station, U. S. Bureau of Mines, Berkeley, California.

[3] Anderson, THIS JOURNAL, 52, 2296 (1930).

and Schwers[4] between 20 and 90°K., a few mean specific heats by Russell[5] from about 140 to 300°K., two determinations by Dewar[6] and a determination by Richards and Jackson.' The results of previous investigators are summarized and compared with the author's value in Table II.

TABLE II

THE GRAM ATOMIC HEAT CAPACITY OF SILICON

T, °K.	Mean T, °K.	C_p	Investigator	From author's curve
20.1		0.031	Nernst and Schwers	0.042
28.2		.086		.123
39.7		.248		.336
53.1		.548		.630
65.6		.826		.920
89.8		1.524		1.495
82.1 to 192.7	137.4	2.44	Russell	2.61
273.1 to 194.9	234.0	4.10		4.16
319.0 to 275.1	297.0	4.84		4.74
20 to 77 (melted)	48.5	0.86	Dewar	0.53
20 to 77 (cryst.)	48.5	0.77		
85 to 293	189	3.34	Richards and Jackson	3.55

The results of Nernst and Schwers, the mean values of Russell and the mean value obtained by Dewar for the crystalline silicon are shown in Fig. 1. Richards and Jackson's result is not plotted as their temperature interval was unusually large. The results obtained in this Laboratory on the heat capacity of silicon expressed in gram calories (15°) per gram atom are given in Table III, and also are shown graphically in Fig. 1. In chang-

TABLE III

HEAT CAPACITY PER GRAM ATOM OF SILICON

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
61.2	0.811	161.4	3.093	237.5	4.151
65.1	.974	164.3	3.116	241.4	4.236
75.0	1.160	165.8	3.187	246.6	4.299
88.4	1.453	179.5	3.406	253.3	4.431
98.8	1.695	186.9	3.539	258.2	4.383
116.7	2.162	192.5	3.576	265.9	4.893
129.8	2.443	196.0	3.678	283.3	4.680
133.6	2.519	199.2	3.735	287.0	4.703
145.5	2.760	205.3	3.807	290.4	4.685
157.1	2.983	213.6	3.901	294.5	4.671
158.8	3.020	222.8	4.011	296.3	4.652

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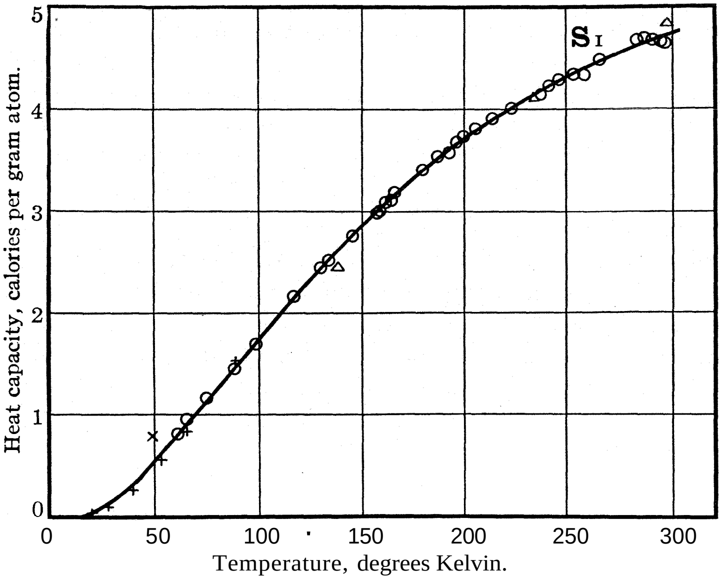
[4] Nernst and Schwers, "Berlin Akademie der Wissenschaften Sitzungsberichte," 355 (1914).

[5] Russell, *physik.* Z., 13, 59 (1912).

[6] Dewar, *Proc.* Roy. *Soc.* (London), A89, 158 (1913).

[7] Richards and Jackson, Z. *physik.* **Chem.,** 70, 414 (1910).

ing joules to calories for the results of this table, the factor[8] 1/4.184 was used. The calculations were made on the basis of Si = 28.1. The accuracy of the data do not warrant correction for the impurities present, none of which are significant except the silicon dioxide, and the mass content and equivalent heat corrections nearly balance out in this case.



○, Anderson; +, Nernst and Schwers; A, Russell; X, Dewar.

Fig. 1.—The heat capacity of silicon in calories per gram atom.

Calculation of Entropy.—The entropy was calculated in the conventional manner. The experimental heat capacity curve on a C_p–log T chart was extended below the lowest measurement and made to coincide with the Debye function having the parameter $\Theta = 441$. The results of these entropy calculations are

Extrapolated (0–56.2) °K.	0.288
Graphical (56.2–298.1)	4.237
Total	4.52 ± 0.05 E. U.

The result, 4.5, differs by 0.2 E. U. from the value 4.7 given by Lewis and Randall[9] calculated from the meager data existing at that time, and is thought to be of better accuracy, especially in view of the high purity of the author's sample.

The author wishes to thank R. W. Millar for making three of the experimental determinations.

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[8] "International Critical Tables," Vol. I, p. 24.

[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 464.

Summary

The true heat capacity of silicon from 60 to 300°K. has been determined and its entropy at 298°K. calculated as 4.52 entropy units.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY AND THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, ALBANY MEDICAL COLLEGE]

THE FORMATION OF VITAMIN D BY MONOCHROMATIC LIGHT[1]

BY ABRAHAM LINCOLN MARSHALL AND ARTHUR KNUDSON

RECEIVED FEBRUARY 17, 1930 PUBLISHED JUNE 6, 1930

It has now been demonstrated fairly conclusively by the work of Rosenheim and Webster[1a] and of Hess and Windaus[2] that ergosterol is the parent substance and apparently the only sterol from which it is possible to make a preparation by irradiation with light which is effective in curing rickets. Previous to this work it was thought that cholesterol was the provitamin, but this activity has been shown to be due to the presence of about 0.05% of ergosterol in the cholesterol, which can be destroyed by brominating the cholesterol.[1,2,3]

Several investigators have experimented with the effect of monochromatic light on cholesterol. Hess and Anderson,[4] using a quartz monochromator, concluded that the upper limit of wave length which gave any effect was 3130 Å. Light of wave length 2800 and 3020 Å. produced material of marked potency. The energy density of radiation was 3.9 ergs per second per sq. mm. but the total dose is not given. Sonne and Rekling[6] have rayed rats directly with lights of various frequencies obtained from a monochromator. The wave lengths used were 366, 313, 302–297, 280, 265, 254, 248 and 227–220$\mu\mu$ obtained from a mercury arc. The area rayed was 8.1 sq. cm. and the energy density varied from 5–0.3 $\times$ 10^{-4} g. calories per sq. cm. per minute. All the rats were rayed for thirty minutes daily. In the range 302–254$\mu\mu$ the rats were exposed to approximately 1.3 X 10^6 ergs daily and were protected from rickets by the light when fed McCollum's ricket producing diet; 248$\mu\mu$ and 240$\mu\mu$ were found to have less effect and 227$\mu\mu$ no effect. However, in the last three cases the energy used was considerably less than in those cases giving complete protection; 313$\mu\mu$ had only a doubtful action and

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[1] A report of this work was presented at the Swampscott Meeting of the American Chemical Society, September, 1928.

[1a] Rosenheim and Webster, *Biochem.* J.,21, 389 (1927).

[2] Hess and Windaus, *Proc Soc. Exptl. Biol. Med., 24,* 461 (1927).

[3] Windaus and Hess, *Nachr. Ges. Wiss. Gottingen, Math.-phys. Klasse, 175* (1926).

[4] Hess and Anderson, *J. Am. Med. Assocn., 89,* 1222 (1927).

[5] Sonne and Rekling, *Strahlentherapie,* 25, 552 (1927).

366 no effect whatever. Fosbinder, Daniels and Steenbock[6] have rayed solid cholesterol with light of varying wave lengths obtained from a monochromator. The cholesterol was fed to rats having severe rickets over *a* ten-day period. The animals were killed and healing was detected by means of the line test. The minimum amounts of energy required to produce a measurable effect were as follows: 234 ergs at 2650 Å., $>$ 350 ergs at 2537 Å., 1170 ergs at 2800 Å. and 2730 ergs at 3020 Å.

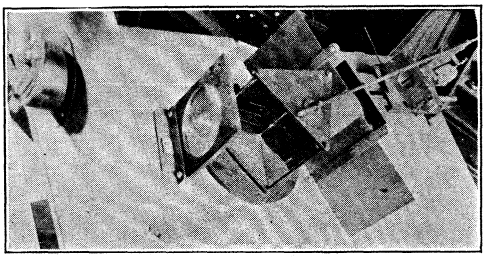

Fig. 1.—The monochromator.

In a subsequent paper[7] it was found that the quantity of radiant energy necessary to form an amount of vitamin D from ergosterol sufficient to cause demonstrable deposition of calcium in the bones of a rachitic rat was constant over the range 256–293$\mu\mu$, 700–1000 ergs being necessary.

Apparatus

A monochromator similar in design to that described by Harrison and Forbes[8] was used in this investigation.

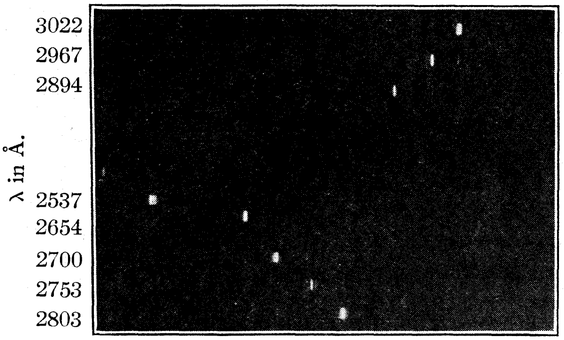

Fig. 2.—Photograph to show purity of monochromatic light obtained.

The 60° prism was made from fused quartz 135 X 135 X 135 mm. The fused quartz lenses had a ratio of focal length to diameter of 2 at 2800 Å. There was a considerable amount of spherical aberration with both lenses and this was corrected in part by the diaphragm shown in Fig. 1. This spherical aberration is largely responsible for

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[6] Fosbinder, Daniels and Steenbock, THIS JOURNAL, 50, 923 (1928).

[7] Kon, Daniels and Steenbock, *ibid.*, 50, 2573 (1928).

[8] Harrison and Forbes, J. Opt. *Soc.* Am, 10, 1 (1925); see also Villars, THIS JOURNAL, 49, 326 (1927).

the considerable amount of continuous background shown in Figs. 3, 4 and 5 and for most of the impurity present in the individual lines in Fig. 2. The collimator slit was made from invar and curved slightly in order to neutralize distortion in the optical system and to obtain a vertical image at the telescope slit. Both slits were adjustable as to width. A linear Moll thermopile was mounted behind the rear slit and connected to a Moll galvanometer mounted on a Julius suspension. The lamp and scale were placed two meters from the galvanometer and the latter was found to have a current sensitivity of 10^{-9} amp. for 1 mm. deflection with a current of 1 amp. in the magnet coil. A photograph of the monochromator is given in Fig. 1. Figure 2 gives a series of spectrographs taken with a large Hilger quartz spectrograph of the light incident on the telescope slit of the monochromator at various settings using a mercury arc as light source. The times of exposure at the different settings were chosen to give roughly the same exposure on the plate for each setting, which thus gives a good idea of the degree of purity of the light obtained. The dispersion of the instrument was found to be given by the equation

$$\lambda = 1100 + \frac{11\,800}{d}$$

where d is a scale in cm showing position of telescope slit

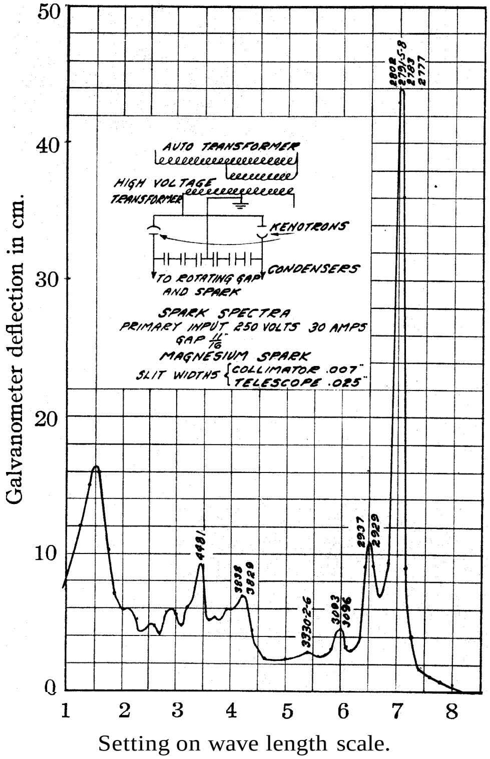

Fig. 3.—Energy distribution of magnesium spark.

Energy Calibration.—The thermopile–galvanometer system was calibrated in absolute units by means of a standard carbon lamp No. C63 supplied by the Bureau of Standards. The thermopile mounted behind the telescope slit was set at 2 meters from the lamp. The slit width was 1.22 mm. Table I gives the results of the calibration.

TABLE I

CALIBRATION OF THERMOPILE

Length of telescope slit, 27 mm. Area of slit, 33 sq. mm. 1 cm. scale deflection = $83 \times (10)^{-7}$ watt. Incident on slit = 83 ergs per second.

Lamp current, amp.	Energy incident on slit per sq. mm.	Scale reading	Incident energy/sq. mm. per cm. deflection
0.300	$47.0\ (10)^{-8}$ watt	1.85	$25.4\ (10)^{-8}$
0.400	$85.8\ (10)^{-8}$ watt	3.53	$24.3\ (10)^{-8}$
		Average	$24.8\ (10)^{-8}$

Light Sources.—In order to obtain monochromatic light of high intensity at the various wave lengths, a number of light sources were used and a brief summary of the energy distribution curves of these sources will not be out of place at this point. A magnesium spark operated by means of a rotating gap from a high voltage direct current outfit illustrated in Fig. 3 was used as a source of 2900 Å. as was also the high pressure mercury arc. The spark was operated with an energy input of 7.5 kw. Variation of the number of breaks per minute between 3600 and 24,000 made no difference in the light intensity. The capacity used was 0.30 mf.; when this was reduced to 0.002 mf. the spark would only take an input of 2.25 kw. at the original setting of the electrodes and this gave about 16% of the original light intensity. The electrodes were cylinders of magnesium $^5/_8''$ in diameter tapered at the end to an area $^1/_8'' \times {}^1/_4''$ and operated without any artificial cooling over long periods of time with very small wastage of magnesium. The energy distribution for this source is remarkable in having such a very large portion of the energy concentrated in the group of lines about 2790 Å. A number of experiments were made raying the material directly with the light from the spark. Since the absorption of ergosterol is very small for wave lengths longer than 3100 Å., this means that all the energy absorbed lies in the region 3095, 2930 and 2790 Å.; 3095 contributes 4%, 2930, 18% and 2790, 77%. This amounts to approximately monochromatic light of wave length 2800 Å. as far as ergosterol absorption is concerned.

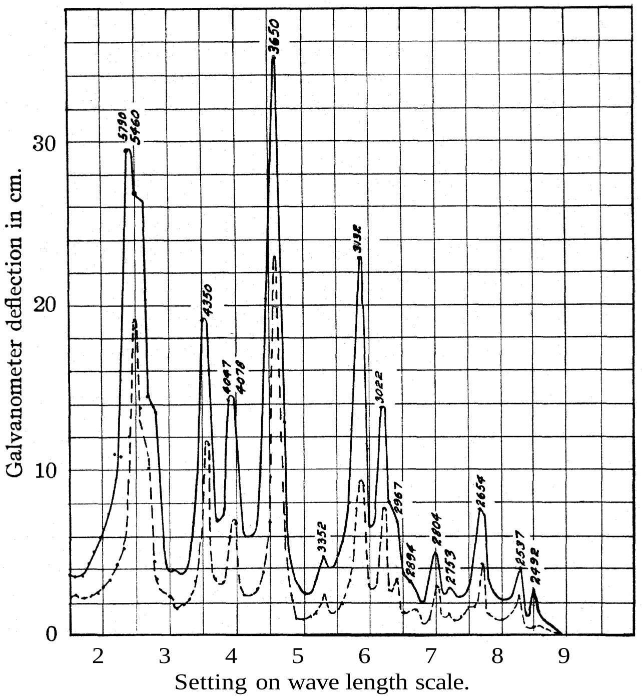

Fig. 4.—Energy distribution in mercury arc. Rating: 83 volts, 6.0 amps. Lower curve: front slit, 0.007"; rear slit, 0.010". Upper curve: front slit, 0.015"; rear slit, 0.010". Arc length, 8.5 cm.

Figure 4 illustrates the manner in which the intensity varies as the slit widths of the monochromator are changed and also give the energy distribution for the high-pressure mercury arc. From this source bands at 3022 and 2804 Å. were used. Figure 5 illustrates the energy distribution of a low-pressure mercury arc and shows that the 2536 Å. line is very strong under these conditions. It was used as a source of this wave length. A subsequent paper will discuss in detail the characteristics of this source.

A quartz cadmium arc was constructed as a source of 2300 Å. The anode consisted of an all-tungsten cylinder and a hot tungsten cathode was used as a source of electrons. The main arc tube was about 6″ long and 0.25" inside diameter. Great care was taken in baking out the lamp and distilling in cadmium to avoid any contamination by mercury. About 2 mm. pressure of neon was admitted to the arc before it was sealed off. The bulbs containing the anode and cathode were heated so that the coldest portion was at 365". This arc was operated continuously at 4 amps. and 64 volts for almost a week and showed no change in intensity at 2300 **A.** as measured by the monochromator.

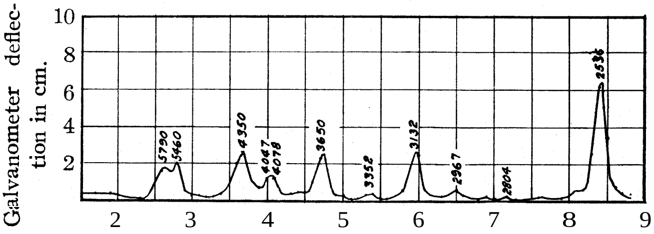

Fig. 5.—Energy distribution for low-pressure mercury arc. Mercury pressure, 0.0036 mm.; rating, 32 volts, 28.8 amps.; arc length, 30 cm.; front slit, 0.007"; rear slit, 0.025".

Experimental Technique.—A solution of ergosterol in absolute alcohol containing 20 mg. per 100 cc. of solution was used for all the work to be reported. A quartz cell 0.5 cm. thick by 1.0 cm. wide by 3.0 cm. high was used with two sides made from ground and polished plates. The cell was placed in contact with the rear slit of the monochromator and the light path through the solution was 0.5 cm. long. Of the light incident on the slit, 5% was reflected at the polished quartz surface of the cell and the remainder passed into the solution. From the absorption curve[9] for this solution given in Fig. 6, it is possible to calculate the percentage of the light incident on the slit which was absorbed by the solution; 40% was absorbed at 3022 Å., 93% at 2800 Å., 76% at 2536 Å. and **73%** at 2300 Å.

The test for antirachitic potency of the different preparations was carried out with rats, using the technique which was reported in a previous paper from these Laboratories.[10]

In brief, rickets was produced in rats by feeding them the Steenbock rachitic diet 2965 for a period of three weeks; after this time had elapsed they had usually developed a marked and uniform degree of rickets. X-

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[9] These absorption curves were made by the courtesy of the Eastman Kodak Research Laboratory.

[10] Knudson and Moore, J. *Biol. Chem.*, **81**, 49 (1929).

ray pictures were taken of the rats before starting the experiment. The experimental period lasted for twenty-one days and x-ray pictures were again taken at the end of the period and in many cases after seven days. Comparisons were made with the radiograph, taken at the beginning of the experimental period, to judge the degree of healing. A "beginning healing" is indicated when there is a scattering of calcium salts which cast a hair-line shadow in the epiphyseal region; "moderate healing" when a narrow band shows in the epiphyseal area; advanced "healing" when about two-thirds of the epiphyseal area is filled up with deposit; and "complete healing" when the epiphyseal region is almost closed up, showing only a narrow cartilaginous area and the bone approaches its normal appearance. The radiographic technique as developed in our Laboratory is in most cases as sensitive as the line test; however, there are a few instances in which we have observed that the line test showed perceptible healing which was not visible by the radiograph.

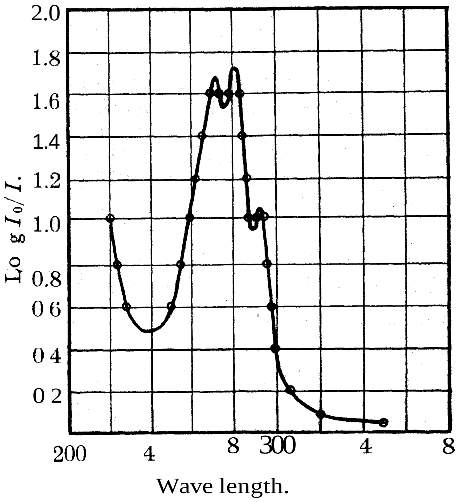

Fig. 6.—Absorption of ergosterol: 1 mg. in 10 cc. of absolute alcohol, 1-cm. layer.

Before irradiation with monochromatic light the ergosterol was dissolved in absolute alcohol and the alcoholic solution after irradiation was then added to a measured amount of olive oil. The alcohol was distilled off from the olive oil under reduced pressure, below a temperature of 60°. The test preparation dissolved in olive oil was then diluted with appropriate amounts of oil in order to have a concentration suitable for administration to the rat. In all cases we have diluted the preparations so that the dose required for administration was dissolved in 0.05 cc. of oil, and this was given directly into the mouth by means of a capillary pipet.

In arriving at the maximum potency of the preparation we would start with the dilution which we considered would give a beginning or moderate healing. We then diluted the preparations in the order of five-fold and tested them until we found a preparation that would give a beginning healing, and one that was negative. In certain instances we were unable to carry this procedure to the extinction point due to a lack of material, because of the fact that some of these preparations were radiated as long as seven days continuously, and the amount that we could irradiate at one time was 0.3 mg.

Results

Experiments were first made on the effect of varying light intensity on the minimum daily dose of radiated ergosterol necessary to show the first incidence of healing. In all exposures in a given experiment the product of intensity and time was kept constant. If the production of the vitamin varies directly with the light intensity, the minimum dose obtained from all these preparations should be constant. The magnesium spark was used as a light source and the light intensity varied by a hundredfold by moving the specimen progressively further from the source. Table II gives the result of these experiments.

TABLE II

EFFECT OF LIGHT INTENSITY ON PRODUCTION OF VITAMIN D

Time of radiation, seconds	Distance from spark. cm.	Approx. energy[11] absorbed, ergs	Daily minimum dose, mg.
2	30	2000	1/2500
20	100	2000	1/2500
200	300	10,000	1/500

In ensuing experiments the wave length was varied from 3022 Å. to 2300 Å. and the time of exposure varied 30,000-fold in some cases The data are given in Table III. Column 1 gives the light incident per second on the rear slit of the monochromator; Col. 4 the total energy absorbed by **0.3** mg. of ergosterol present in the cell during the period of radiation; Col. 6 the minimum amount of the radiated ergosterol which had to be fed daily to show perceptible healing by a radiographic method after three weeks and Col. 5 gives the amount of energy received by the ergosterol which produced this healing effect; this energy is thus the minimum amount necessary to produce a perceptible effect. Part of the experiments with 2800 Å. were performed using the magnesium spark as a source without recourse to monochromator; in this case the energies are estimated by comparison with other experiments using the monochromator.

Figure 7 shows a plot on logarithmic paper of the results of Table III. The minimum daily dose is shown as a function of the total energy absorbed by the constant amount of ergosterol which was irradiated for each experiment. The log–log plot is used to condense the wide range covered into a single plot. In the initial stages of irradiation the minimum dose varies inversely with the amount of energy absorbed; this shows that the amount of vitamin D formed is directly proportional to the light absorbed. With prolonged irradiation this linear relationship no longer holds, the net amount of vitamin D obtained being smaller for each succeeding period and finally a stage is reached where there is a loss of the

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[11] This is the total energy absorbed by the ergosterol which was fed to the rat over a period of 21 days and which produced a beginning healing.

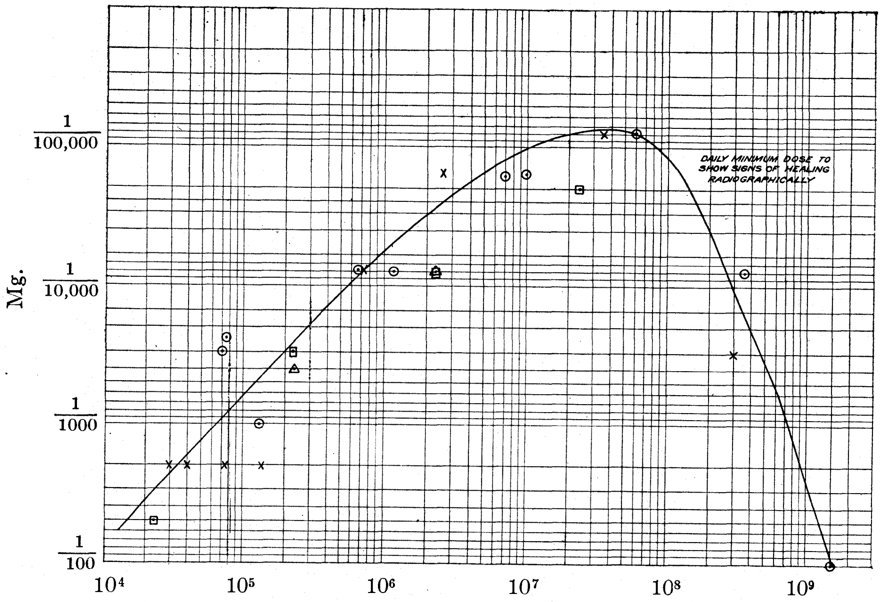
TABLE III

EXPERIMENTAL DATA

Light intensity, ergs/sec.	Time of exposure, sec.	λ in Å.	Total energy absorbed in cell, ergs	Minimum energy received by rat in 3 weeks	Daily minimum dose, mg.
2500	240	3022	$2.4(10)^5$	16,000	1/1000
2500	2400	..	$2.4(10)^6$	13,000	1/12,500
465	19,800	2800	$9.2(10)^6$	9,300	1/62,500
3850	20		$7.7(10)^4$	1,700	1/3000
1070	120		$1.2(10)^5$	8,000	1/1000
1070	1200		$1.2(10)^6$	6,400	1/12,500
	2	Mg	$7(10)^4$	2,000	1/2500
	20	spark	$7(10)^5$	4,000	1/12,500
	200	direct	$7(10)^6$	8,000	1/62,500
	2000		$7(10)^7$	40,000	1/125,000
	14,400		$3.5(10)^8$	$1.9(10)^6$	1/12,500
	57,600		$1.4(10)^9$	$9.3(10)^8$	1/100
880	60	2536	$4(10)^4$	5,300	1/500
3300	20		$2.9(10)^4$	3,800	1/500
3300	95		$1.4(10)^5$	3,800	1/2,500
3300	1,800		$2.6(10)^6$	2,600	1/62,500
3400	10,800		$3.7(10)^7$	20,000	1/125,000
3400	86,400		$3.0(10)^8$	$8(10)^6$	1/2,500
3400	590,000		$2.6(10)^9$	....	<1/100
2600	30		$7.8(10)^4$	5,000	1/1,000
2600	300		$7.6(10)^5$	4,000	1/12,500
400	60	2300	$2.3(10)^4$	6,100	1/250
400	600		$2.3(10)^5$	6,100	1/2,500
400	6000		$2.5(10)^6$	13,300	1/12,500
400	60,000		$2.4(10)^7$	24,000	1/62,500

vitamin with further irradiation. It is thus evident that we are dealing with two simultaneous reactions of light: first, a synthesis of vitamin D from ergosterol and second, a destruction of the vitamin. As the reaction proceeds the ergosterol concentration is decreasing and the vitamin D increasing, so that in the later stages the destructive role of the light predominates. We have only carried out prolonged irradiations at 2800 Å. and 2536 Å., since these experiments require intense sources of light to enable one to carry them out in a reasonable time; at 2536 Å. the longest period of irradiation was seven days and to obtain a similar amount of energy at 2300 Å. would have taken five weeks. In the two cases investigated the results were identical and there is no reason to assume that the results with other frequencies would have been different. Vitamin D has to absorb light in the same wave length region as ergosterol in order to be destroyed by light of the same frequency as that which forms it. About 10^8 ergs of light energy were necessary to produce the maximum concentration of vitamin D in 1 mg. of ergosterol dissolved in 5 cc. of absolute alcohol. From these results it is now possible to state that a concentration of vitamin D corresponding to a minimum daily dose of 1/125,000 mg. is the maximum concentration which can be produced by direct irradiation of ergosterol. The results for all the wave lengths are identical within the accuracy of the biological method used for testing.

Tanret[12] gives the formula $C_{27}H_{42}O \cdot H_2O$ for ergosterol, which gives it a molecular weight of 400. One milligram of ergosterol contains 1.5×10^{18} molecules. A quantum of 2800 Å. contains 7 X 10^{-12} ergs. Two thousand ergs of 2800 Å. absorbed by ergosterol and fed to a rat with rickets over a period of three weeks produced a perceptible healing. This amount of energy contains 3 X 10^{14} quanta. The rat received 1/150 mg. of the irradiated material over a period of three weeks or about 10^{16} molecules. The purest preparation of vitamin D which has been prepared by Bourdillon and Webster[13] produced a perceptible healing with 1/20,000 mg. fed over a three-week period, so that if we assume this preparation to have been pure vitamin D, our material in this case contained about 0.7% of the vitamin or approximately 10^{14} molecules. This means that 1 quantum produces on the average 0.3 molecule of vitamin D. In another experiment where a concentration of 16% vitamin D was reached, 3.7 X 10^{17}



Total energy in ergs for 0.3 mg. of material.

△, 3022 A°; ×, 2536 A°; ⊙, 2800 A°; ⊡, 2300 A°.

Fig. 7.

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[12] Tanret, *Compt. rend.*, **147**, 75 (1908).

[13] Bourdillon and Webster, *Proc.* Roy. *Soc.* (London), **104B**, 561 (1929).

quanta produced 7.2×10^{16} molecules of the vitamin, giving a quantum efficiency of 0.20. Fourteen-fold increase in the amount of radiation received by the sample increased the vitamin D concentration to 35%; in other words, 5.3×10^{18} quanta produced 16×10^{16} molecules of vitamin D instead of 1×10^{18} molecules as calculated from the quantum efficiency in the previous experiment. There were only 4.5×10^{17} molecules of ergosterol present in the cell; this means that the quantum efficiency for the transformation of vitamin D to some inert substance is greater than for its production from ergosterol. It is evident from these experiments that vitamin D must itself possess a strong absorption band in the same region as ergosterol, contrary to the work of Heilbron, Morton and Kamm.[14] Since this work was completed two papers[15,16] have been published giving experimental proof that the absorption spectrum of vitamin D occurs in the same spectral region as that of ergosterol. Smakula has shown that a solution of ergosterol from which air is not excluded completely loses its characteristic absorption spectrum after standing for a few months. He has measured the absorption spectrum of a solution of ergosterol during the course of radiation and found at first a slight decrease in absorption and then an increase followed later by a decrease and disappearance of the characteristic absorption. On the basis of a rather questionable rate of disappearance of ergosterol he calculates the absorption spectrum for vitamin D with two maxima at 293 and $260\mu\mu$. Bourdillon and Webster have examined the absorption spectra of irradiated ergosterol solutions both before and after the removal of ergosterol and have found maxima at 270 and $280\mu\mu$ which they believe to be due to vitamin D. The material with an absorption maxima at $240\mu\mu$ is formed by radiation from vitamin D and has no antirachitic action; it in turn is changed by further irradiation to a substance showing no specific absorption. The extinction coefficient for a substance which they think is mainly vitamin D is 40% greater than that of ergosterol and the absorption curve is practically the same shape. They have prepared a material whose biological action can be detected radiographically in doses of 1/400,000 mg. daily and we have assumed that this material is pure vitamin D in calculating quantum efficiencies in this paper.

Summary

1. Several intense sources are described for obtaining monochromatic light of various wave lengths.

2. The rate of production of vitamin D from ergosterol is proportional to the first power of the light intensity.

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[14] Morton, Heilbron and Kamm, *J. Chem. Soc.*, 2000 (1927).

[15] Smakula, *Nach. Ges. Wiss. Göttingen, Math.-phys. Klasse*, 49 (1928).

[16] Bourdillon, Pischmann, Jenkins and Webster, *Proc. Roy. Soc.* (London), **104B**, 561 (1929).

3. The rate of production of vitamin D is directly proportional to the number of light quanta absorbed by ergosterol and independent of the wave length of the light used.

4. Vitamin D absorbs in the same wave length region as ergosterol and is destroyed by light of the same wave length as that which forms it.

5. The highest concentration of vitamin D which can be produced by direct irradiation of ergosterol is 35%. This is an absolute maximum and the probable value is lower.

6. The quantum efficiency is 0.3 molecules of vitamin D per quantum of light absorbed.

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REDUCTION OF METAL OXIDES BY HYDROGEN

BY GUY B. TAYLOR AND HOWARD W. STARKWEATHER

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A common method for the preparation of metal catalysts consists in first preparing a finely divided oxide and then reducing the oxide with hydrogen. Usually the lower the temperature of reduction the greater the catalytic activity. Low temperature means a slow process of reduction. The present article is concerned with a new method for studying the rate of reduction. Nearly all prior work in this field has been done by passing hydrogen over the heated oxide and collecting and weighing the water formed at definite time intervals. The present method involves following the rate of reduction by measuring the volume of hydrogen consumed.

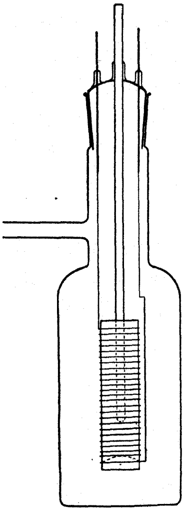

Fig. 1.

Method.—The essential feature of the apparatus is shown in Fig. 1. Platinum wire was wound on a mica cylinder to make a small electric heater, 2 by 6 cm. This heater was suspended on stout nickel wires in a pyrex vessel. The nickel wires were brazed to tungsten wires for sealing through the ground stopper of the vessel. These stout wires served both as supports and electrical leads. A small glass tube sealed to the stopper extended to the middle of the heater and served as a well for a fine-wire chromel–alumel thermocouple. The bottom of the mica cylinder was closed with a piece of platinum gauze wedged on the inside.

The rest of the apparatus consisted of a compensated gas buret, electrolytic hydrogen generator, and Hyvac pump. Electrolytic hydrogen was generated from sodium hydroxide with nickel electrodes, passed over a glowing platinum wire to free it from traces of oxygen, and dried by Dehydrite. Suitable stopcocks were prbvided so that the buret could be refilled rapidly and repeatedly during the course of a run.

The heater was charged by putting a layer of porcelain chips in the bottom, then the oxide, usually three cubic centimeters, and more chips on top. This insured a bed of reacting material in the middle of the heater surrounding the thermocouple hot-junction. The oxide was then heated in air and finally in a vacuum before admitting hydrogen to the vessel in order to drive out moisture and adsorbed gases. During a run the vessel was immersed in a bath at constant temperature, usually running tap water. The temperature of the bath definitely fixed the partial pressure of water vapor during a run just as soon as any of the water formed by the reduction condensed on the walls. Runs in an atmosphere of dry hydrogen were made by surrounding the vessel with a bath of solid carbon dioxide in methanol or by putting phosphorus pentoxide directly in the vessel.

The heat capacity of the charge and heater was only a few calories, so that it was possible to raise the temperature to 450° in three or four minutes with the current required to hold that temperature during a run. The heating current was drawn from a storage battery, and by merely keeping an ammeter at a definite mark, constant temperature was easily maintained.

In starting a run the gas buret was only partly filled with hydrogen, to allow for expansion on heating the charge. Correction for the expansion was obtained by a preliminary calibration with porcelain chips in the heater. Table I shows the complete data of a typical run. In this case the correction for expansion on heating the sample from 25 to 400° was 35 cc.; from 400 to 450° the correction was 3.5 cc.

TABLE I

RATE OF REDUCTION OF NiO, SUPPORTED (0.6 GRAM NICKEL)

Run No. 15. Bath temperature, 21.5°

Time	°C.	Heating current, amp.	Buret readings Cc.	Buret readings Refill, cc.	Consumption of H_2, Minutes	Consumption of H_2, cc. H_2, 25°C., 1 atm.
9:51	25	5.30	7.0			
9:53	300	5.30	23.1			
9:55	390	5.30	7.6		4	34.4
9:56	400	5.30	0	50.2		
9:58	400	5.30	34.2		7	58.0
10:01	400	5.30	23.1		10	69.1
10:04	400	5.30	13.8		13	78.4
10:09	400	5.25	4.1	50.0	18	88.1
10:19	400	5.25	35.6		28	102.5
10:29	400	5.25	26.9		38	111.2
10:39	400	5.25	21.0		48	117.1
10:49	400	5.25	16.7		58	121.4
11:00	400	5.25	13.4		69	124.7
11:17	400	5.22	8.5		86	129.6
11:32	400	5.22	5.3		101	132.8
11:47	395	5.22	2.5		116	135.6
11:57	395	5.22	1.4	49.2	126	136.7
12:50	395	5.22	41.9		179	144.0
1:30	395	5.70	38.5		219	147.4
1:33	450	5.70	42.0			
1:40	450	5.65	36.2		229	153.2
1:45	450	5.65	32.0		234	157.4
1:55	450	5.65	26.3		244	163.1
2:06	450	5.65	21.7		255	167.7
2:26	450	5.65	15.7		275	173.7

In most cases the samples were prepared as granules 8- to 14-mesh. Unless otherwise stated all reductions were carried out in hydrogen saturated with moisture at 10 to 25°, *i. e.*, the reaction vessel was kept in running tap water. The volume of hydrogen measured for any reduction experiment includes that adsorbed by the sample above room temperature or desorbed on heating. In most cases such effects are negligible.

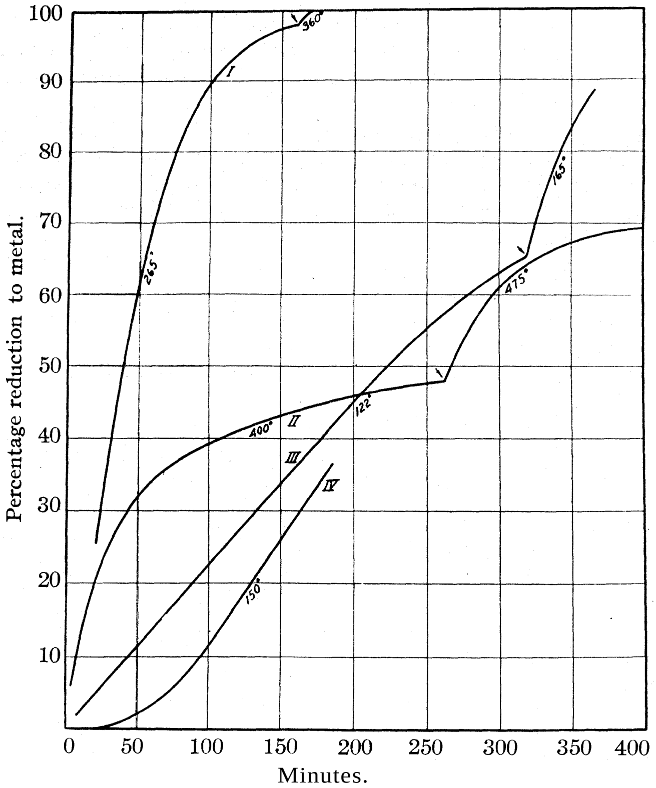

Fig. 2.—Curve I, NiO by ignition of the oxalate at 400°; II, NiO on kieselguhr; III, CuO by ignition of the oxalate; IV, CuO, wire form; ↓, temperature change.

Reduction of Single Oxides.—In Fig. 2 are shown some representative results with nickel and copper oxides in hydrogen saturated with water vapor at about 20°. Nickel oxide on a kieselguhr support proved much more difficult to reduce than a sample of unsupported material.[1] Whether the curve for copper oxide is autocatalytic in character depends largely on the individual sample. The work of Wright, Luff and Rennie[2] and of Pease and Taylor[3] shows that the reduction occurs at the metal–metal oxide

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[1] Rideal and Taylor, "Catalysis in Theory and Practice," The Macmillan Co., London, 1926, p. 242.

[2] Wright, Luff and Rennie, *J. Chem. Soc.*, **33,** 1 (1878); **35,** 475 (1879).

[3] Pease and Taylor, THIS JOURNAL, 43, 2179 (1921).

interface. If, at the beginning of the reduction, relatively few interfaces are developed, a curve showing an induction period followed by autoacceleration is obtained as with the wire-form sample. The result with the other sample of copper oxide, prepared from the oxalate, may be explained on the assumption of the initial formation of a large number of interfaces. One of the samples checks the observations of Pease and Taylor and the other those of Larson and Smith.[4] The mechanism of nickel oxide reduction is probably the same as that for copper oxide."

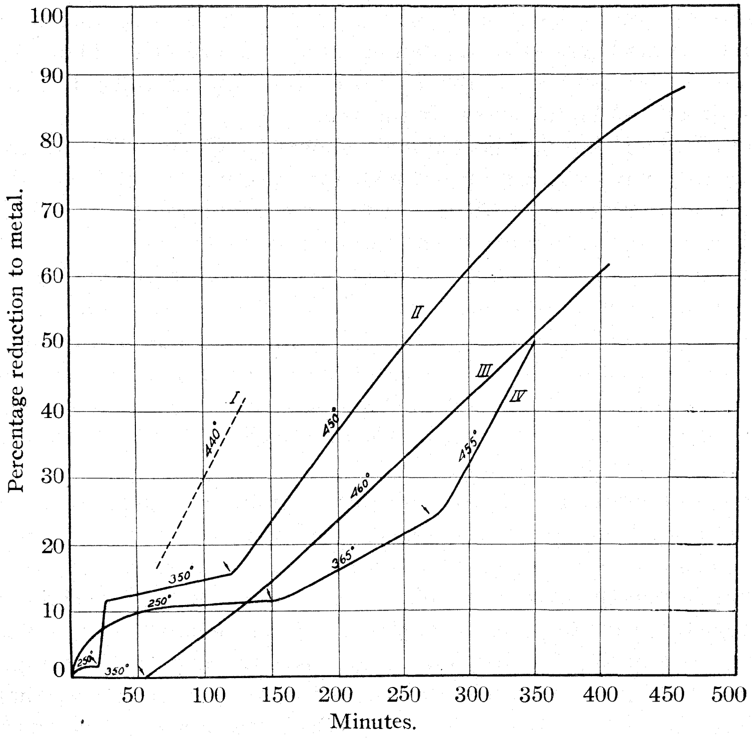

Fig. 3.—Ferric oxides. Curve I, Sample XII in dry hydrogen; II, Sample XII in wet hydrogen; III, Sample XII ignited at 900°; IV, Sample XXVII; ↓, temperature change.

Figure 3 shows some representative results on the rate of reduction of ferric oxide. Sample XII was prepared by precipitating a solution of ferric nitrate (10 g. of $Fe(NO_3)_3 \cdot 9H_2O$ per 100 g. of H_2O) with 7% ammonium hydroxide solution, washing free from nitrate, and drying at 150°. Sample XXVII was prepared from the same salt and alkali four times as

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[4] Larson and Smith, *ibid*., **47**, 346 (1925).

[5] Benton and Emmett, THIS JOURNAL, **46**, 2728 (1924); Pease and Taylor, *ibid.*, **44**, 2179 (1922).

concentrated. Curve II is typical of many preparations of iron oxide gel. There is a slight reduction at 250°. On raising the temperature to 350° the reduction rises sharply to 11%, which corresponds to reduction of Fe_2O_3 to Fe_3O_4. The rate then slows down. On raising the temperature to 450° the reaction proceeds steadily until all the oxide is reduced to metal. Sample XXVII, precipitated from the more concentrated solutions, reduced to Fe_3O_4 at as low as 250°.

Curve I of Fig. 3 merely shows the slope of the reduction curve at 440° when the reaction vessel was kept at $-78°$ and consequently the vapor pressure of water is less than 0.001 mm. The rate is somewhat faster than when the vessel was kept in running water (Curve II). The rate of reduction at 250 and 350° in dry hydrogen was substantially the same as in wet hydrogen and is not shown in the figure.

The effect of sintering is strikingly shown by Curve III. Sample XII was heated in an electric muffle at 900° for twenty hours and then reduced. There was no reaction at 350°. At 450° the reduction apparently goes to metal since there is no break in the curve at the Fe_3O_4 stage.

Several samples of precipitated oxide were prepared by varying the concentration, the nature of the ferric salt, or that of the alkali. All gave results similar either to Curve II or IV of Fig. 3. The use of potassium instead of ammonium hydroxide did not alter rates of reduction, and this alkali was used for coprecipitating iron and other metals. It will be noted that iron oxide is not reduced autocatalytically. Benton and Emmett[5] have already pointed this out.

Glow Phenomenon.—Nearly all our samples of ferric oxide showed the gel-glow phenomenon[6] when heated in hydrogen. Figure 4 shows the most conspicuous example. The bottom curve shows the reaction rate, the middle one the current supplied the heater, and the top the temperature registered by the thermocouple, all plotted against time. The temperature rise during the first few minutes is extremely rapid, so rapid that the actual temperature reached by the oxide is no doubt higher than that registered by the thermocouple. This effect does not occur when the material is heated in air or in vacuum. Some reduction must occur before the glow can take place. On the other hand, it is possible to reduce the sample by heating it slowly without the glow being evident. While the reaction between hydrogen and ferric oxide to give ferroso-ferric oxide is strongly exothermic, the data given in the figure show conclusively that this reaction is too slow to account for the sudden temperature rise.

Reduction of Mixed Oxides.—Mixed oxides of nickel, copper and silver with iron were prepared by coprecipitation of solutions of sulfate or nitrate

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[6] L. Wohler, *Kolloid-Z.*, 11, 241 (1913). For a discussion of the glow phenomenon; see H. B. Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, 1926, pp. 78–81.

by potassium hydroxide. The precipitates were washed and then electrodialyzed until free of the negative ion. They were dried at 102° before placing in the reduction apparatus. The metals were present in about equal-atom proportions.

Figure 5 shows the effect of added nickel. It is of course impossible to tell which oxide is being reduced the faster, but the slopes of the curves at 450° indicate that the nickel accelerates the final reduction of the iron, since nickel oxide is probably completely reduced before this temperature is reached. Silver and copper gave results of similar character, hence it may be concluded that the presence of a foreign metal interface speeds iron oxide reduction. In the test with silver, silver oxide was dissociated by heating in vacuum before reduction was started.

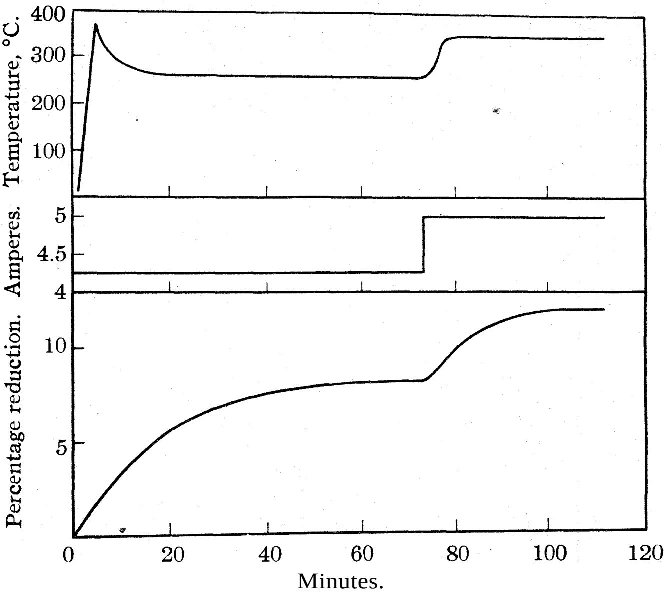

Fig. 4.—Reduction of Fe_2O_3 showing glow phenomenon.

Figure 6 shows the effects of oxides that cannot be reduced by hydrogen to metal. Mixed oxides of iron and chromium and of iron and aluminum, equimolar, were prepared by precipitation. These oxides materially lowered the rate of reduction of the iron oxide at 450°, but if the chromium oxide was mixed mechanically by grinding with ferric oxide, no such effect occurred. Emmett and Love[7] also found that even as small amounts of coprecipitated Al_2O_3 as 1.5% reduced the rate of reduction of Fe_3O_4 to metallic iron.

The curves in Fig. 6 show that the amount of hydrogen consumed at

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[7] Emmett and Love, *J. Phys. Chem.*, **34,** 56 (1930).

360° was greater than that required to reduce the Fe_2O_3 to Fe_3O_4. 'She Cr_2O_3 in the material reduced according to Curve II was prepared from an hydroxide gel made from the sulfate and ignited to 450° in air. It was then of a dark green color, but when reduced by hydrogen it became bright green. This bright green material was used in preparing the mechanical mixture for Curve II.

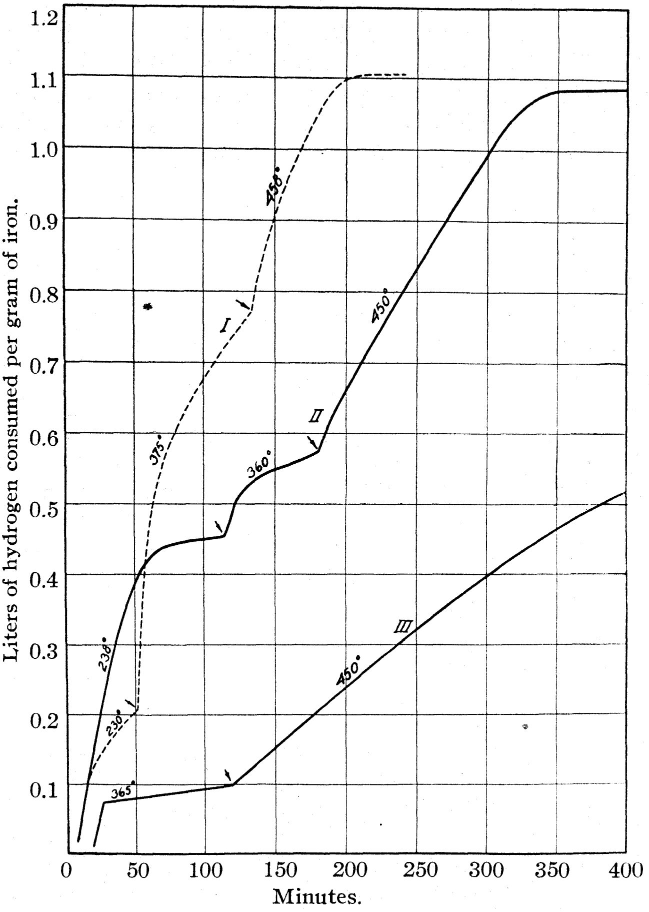

Fig. 5.—Reduction of mixed nickel and ferric oxides. Curve I, NiO–Fe_2O_3 precipitated together; II, NiO and Fe_2O_3 mixed dry; III, Fe_2O_3 alone, Sample XII; ↓ , temperature change.

A 3-g. sample of the coprecipitated Fe_2O_3-Cr_2O_3 used in obtaining Curve I was placed in the apparatus, heated to 250° in vacuum, and cooled to room temperature. Oxygen was then admitted and the sample heated, eventually to 380°; 40 cc. of oxygen was consumed, indicating oxidation of Cr_2O_3. The apparatus was then cooled to room temperature and the oxygen replaced by hydrogen. This oxidized sample was then reduced as usual, giving results similar to those shown in Curve I, save that 80 cc. additional hydrogen equivalent to the above quantity of oxygen was consumed at 238°.

It was further found that pure Cr_2O_3, after being heated in the air, liberated iodine from acidified potassium iodide solution.

Coprecipitated zinc and ferric oxides from nitrate solutions yielded a product difficult to purify. Electrodialysis could not be used to purify this material. The precipitate was washed on a filter and dried at 102°

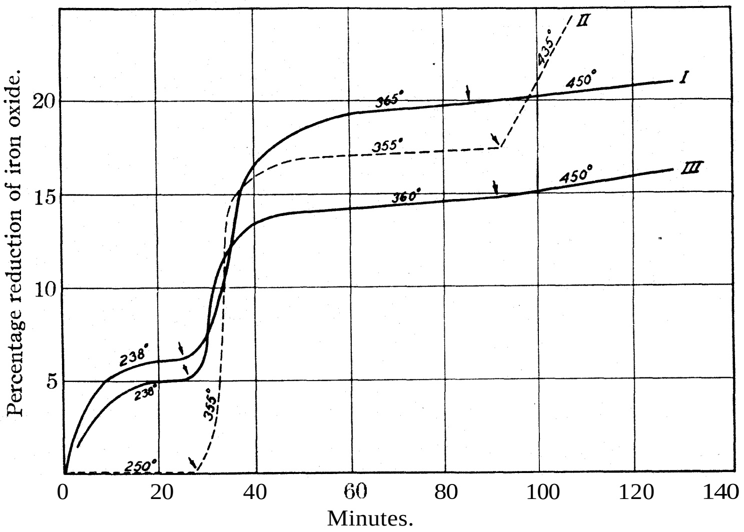

Fig. 6.—Curve I, Fe_2O_3–Cr_2O_3 coprecipitated; II, Fe_2O_3–Cr_2O_3, mechanical mixture; III, Fe_2O_3–Al_2O_3 coprecipitated; t, temperature change.

and analyzed 25% iron. The sample in the reduction apparatus was heated for ninety minutes at 250° and fifteen minutes at 350° to decompose traces of nitrates. Thereafter a reduction experiment gave a curve much like Curve II, Pig. 6. In this case the non-reducible oxide did not slow down reduction of the iron oxide at 450°.

Figure 7 shows the rate of reduction of ferrous oxide. The oxide was prepared by decomposing ferrous oxalate in a vacuum in the reduction apparatus by slow heating to 400°. It did not come in contact with air before reduction. After reduction the iron powder was brilliantly pyrophoric, giving a shower of sparks as it was poured from the heater.

There have been several instances mentioned in the recent literature indicating the reduction of zinc oxide at low temperatures. Rogers[8]

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[8] Rogers, THIS JOURNAL, 49, 1432 (1927).

completely reduced a fused mixture of cuprous oxide and zinc oxide with hydrogen at 300°. Frolich, Davidson and Fenske[9] found evidence for the reduction of zinc oxide in the presence of copper oxide by methanol vapor at 220°. St. John[10] claims to have detected reduction of pure zinc oxide by hydrogen at as low a temperature as 310°. Taylor and Kistiakowsky[11] in their work on adsorption of hydrogen by pure zinc oxide noted gray spots formed on the oxide in a hydrogen atmosphere.

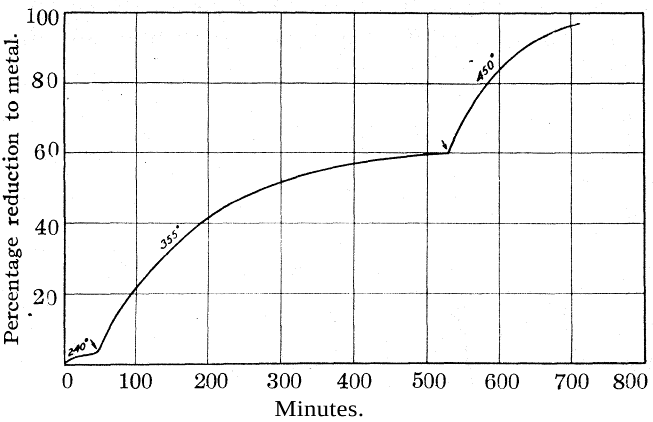

Fig. 7.—Reduction of FeO.

In view of these observations and the fact that zinc oxide is generally considered as non-reducible below the melting point of zinc, calculations were made to determine the conditions under which crystallized zinc oxide might be expected to be reduced by hydrogen.

The free energy of the reaction

$$ZnO(s) + H_2(g) = Zn(s) + H_2O(g) \qquad (1)$$

may be used to calculate the partial pressure of water vapor which must not be exceeded, if the zinc oxide is to be reduced, by the relation

$$\Delta F^\circ = -RT \ln K$$

where $K = [H_2O]/[H_2]$.

The free energy of Reaction 1 was calculated by combining the two reactions

$$ZnO(s) = Zn(s) + {}^1/_2O_2(g) \qquad (2)$$
$$H_2(g) + {}^1/_2(O_2)(g) = H_2O(g) \qquad (3)$$

For Reaction 2,[12]

$$\Delta F^\circ = 83{,}285 + 1.61T\ln T - 0.26 \times 10^{-3}T^2 - 0.645 \times 10^{-7}T^3 - 34.23\,T$$

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[9] Frolich, Davidson and Fenske, *Ind. Eng. Chem.*, *21*, 109 (1929).

[10] St. John, *J. Phys. Chem.*, **33**, 1438 (1929).

[11] Taylor and Kistiakowsky, THIS JOURNAL, 49, 2468 (1927).

[12] Maier and Ralston, THIS JOURNAL, 48, 371 (1926).

and for Reaction 3,[13]

$$\Delta F^\circ = -57{,}410 + 0.94T \ln T + 1.65 \times 10^{-3}T^2 - 3.7 \times 10^{-7}T^3 + 3.92T$$

Adding these equations to get for Reaction 1

$$\Delta F^\circ = 25{,}875 + 2.55\ T \ln T + 1.39 \times 10^{-3}T^2 - 4.345 \times 10^{-7}T^3 - 30.311.$$

then for 300°, $\Delta F^\circ = 18{,}100$ and for 419°, the melting point of zinc, $\Delta F^\circ = 16{,}950$ calories.

In the presence of copper the compound Cu_2Zn_3, a constituent of brass can be formed. The heat capacity of brass is substantially the sum of the heat capacities of copper and zinc entering into its formation, so that ΔH may be taken equal to ΔF°, assuming the heat capacity of brass remains additive all the way to 0°K. The heat of formation of Cu_2Zn_3 is 16,000 calories,[14] so that for each gram-atom of zinc $\Delta F^\circ = -5300$.

The following table gives the calculated partial pressures of water vapor that will prevent the reduction of zinc oxide when the hydrogen pressure is one atmosphere.

EQUILIBRIUM CALCULATIONS

	°C.	ΔF°	K	Water vapor press., mm. Hg
Pure ZnO	300	18100	1.3×10^{-7}	0.0001
Pure ZnO	419	16950	$4\ 4 \times 10^{-6}$	0.0033
ZnO + Cu	300	12800	1.3×10^{-5}	0.01
ZnO + Cu	419	11650	2×10^{-4}	0.15

An experiment was carried out to see if zinc oxide alone could be appreciably reduced under the most favorable conditions possible with our apparatus. Three grams of an especially pure form of zinc oxide was heated in hydrogen at 516° for one hour while the walls of the vessel were cooled to −78° by solid carbon dioxide in methanol. The measured hydrogen consumption was less than 2 cc., which is within the experimental error under the extreme conditions of the test. After the experiment the oxide showed gray spots like those described by Taylor and Kistiakowsky.

Three samples of mixed oxides of copper and zinc were prepared as follows. No. XXIX.—A solution of copper and zinc nitrates was added to potassium hydroxide solution in calculated equivalents to insure complete precipitation. The precipitate was washed on the filter and dried at 102°; analysis: 35.46% Cu, 26.14% Zn. Before reduction it was heated in the apparatus in vacuum to decompose traces of nitrate before hydrogen was admitted.

No. XXXI.—Pure zinc and copper oxides were ground together to pass a 100-mesh sieve and made into pellets in a pill machine; analysis: 40.57% Cu, 39.12% Zn.

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[13] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 485.

[14] Biltz, *Z. anorg. allgem. Chem.*, *134*, 25 (1924).

No. XXXII.—Sample was prepared the same as No. XXXI, then heated in a muffle at 900° overnight and blasted for half an hour in an oxygen–gas flame; analysis: 41.81% Cu, 38.57% Zn.

Sample No. XXIX was heated in wet hydrogen (reaction vessel in water) for 145 minutes, raising the temperature stepwise to 360°. Hydrogen equivalent to CuO in the sample was consumed at 238° and there was no further reduction at 360°. On raising the temperature to 440°, there was a small consumption of hydrogen and then no reaction in thirty minutes. The vessel was then surrounded by the cold bath at −78° and reduction proceeded steadily at 460° at a uniform rate for an hour until the experiment was discontinued. Tests with Sample XXXI under nearly the same conditions were quite similar. With phosphoric oxide in the vessel there was a slow but measurable reduction of the zinc oxide at 365°. After reducing the copper oxide in sample XXXII, condensed water was removed and phosphoric oxide put into the vessel. The reduction of the zinc oxide was then allowed to proceed for eight hours at 350°.

After the three samples were reduced, they were washed with dilute hydrochloric acid to dissolve zinc oxide and examined by x-rays. A chemical analysis of one of the samples was also made. Below are summarized the data of the examination of the reduced samples which prove that alpha brass was formed in all cases.

COMPOSITION OF REDUCED SAMPLES

	X-ray examination		Calcd. % Zn in brass from reduction data	Chemical analysis
Sample no.	Cube edge, Å.	% Zn in brass[a]		
XXIX	3 636	10	12	13% Zn, 84 5% Cu
XXXI	3.643	15	15	......
XXXII	3 625	8	9	......

[a] Calculated by comparison with data for alpha brasses given in "International Critical Tables," McGraw-Hill Book Co., New York, 1926, p. **350,** Vol. **1.**

There thus appears to be nothing mysterious about the reduction of zinc oxide in the presence of copper. It is simply a case of carrying out the reduction in a sufficiently dry atmosphere, to be on the right side of the equilibrium position. A sufficiently dry atmosphere of hydrogen in the case of zinc oxide alone, at temperatures at which it can be reduced in the presence of copper, is difficult if not impossible to realize experimentally.

The authors wish to thank Dr. A. W. Kenney of this Laboratory for making the x-ray examinations, and Dr. H. G. Tanner, also of this Laboratory, for assistance in the free-energy calculations.

Summary

1. A new method for studying the rate of reduction of metal oxides at temperatures below 500° has been described. In this method the volume of hydrogen consumed is measured.

2. Results with this method for nickel, copper, iron and zinc oxides have been presented.

3. Ferric oxide gel is reduced to ferroso-ferric oxide at 350° and to metallic iron at 450°. Ignited ferric oxide is not reduced at an appreciable rate at 350° and goes to metal at 450°.

4. Foreign metal interfaces with iron oxide accelerate the reduction to iron.

5. Alumina and chromium oxide greatly retard reduction of ferroso-ferric oxide.

6. Perric oxide gels show the glow phenomenon in hydrogen at fairly low temperatures, but not in air or in vacuum.

7. The thermodynamics of zinc oxide reduction in the presence of copper have been worked out, giving an explanation in the formation of alpha brass.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 58]

ADSORPTION OF HYDROGEN BY NICKEL AT LOW TEMPERATURES[1]

BY ARTHUR F. BENTON AND T. A. WHITE

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Introduction

Although it is now recognized that the occurrence of catalytic reactions at solid surfaces is intimately connected with the nature and extent of the adsorptions of the reacting species and products, nevertheless, attempts to obtain a quantitative treatment of the relations involved have met with little success. The main difficulty appears to be the lack of an adequate general theory of adsorption at catalytically active surfaces.

Numerous adsorption measurements,[2] especially by Taylor and his co-workers, have shown that adsorption of gases may be accompanied by more or less "activation" of the adsorbed molecules, and that this activation is a prerequisite to any marked catalytic action of the solid. It is known that this activation is conditioned by the chemical rather than the physical properties of the substances involved, but its occurrence is unpredictable theoretically. Experimentally, however, the two limiting types of adsorption, the "secondary" type involving little or no activation and the "primary" type in which relatively great activation occurs, can be

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29–May 3, 1929.

[2] Critical summaries of the extensive work in this field may be found in the following papers: Taylor, *J. Phys. Chem.*, **28**, 897 (1924); **30**, 145 (1926); *Proc. Roy. Soc.* (London), **A113**, 77 (1926); Taylor and Kistiakowsky, *Z. physik. Chem.*, **125**, 341 (1927); Langmuir, THIS JOURNAL, **38**, 2221 (1916); **40**, 1361 (1918).

readily distinguished by the fact that at moderate temperatures and pressures the extent of adsorption is much less dependent on these variables in the latter case than in the former. This fact is interpreted to mean that in primary adsorption even at low pressures the surface is largely covered with a unimolecular or monatomic layer of adsorbed gas, whereas in the secondary type either the unimolecular layer is far from complete or multimolecular layers are formed.

It appeared to us that considerable light might be thrown on these questions by carrying out adsorption measurements on an active catalyst under conditions where one type of adsorption merged into the other, a behavior which might be expected at low temperatures or at high pressures. The present paper deals with the adsorption of hydrogen by active nickel at pressures up to one atmosphere and over a range of temperatures down to 61°K.

The adsorption of hydrogen by nickel at temperatures above 0° has received some attention from numerous investigators. Gauger and Taylor,[3] using temperatures from 25 to 305° and pressures from zero to one atmosphere, found that the adsorption reached a constant value at relatively low pressures, but that this constant value decreased as the temperature was raised. Terwen[4] concluded from these data that at higher temperatures the amount adsorbed approached asymptotically a value half that at lower temperatures, and that the adsorption occurred as atoms at the higher temperatures and as molecules at the lower.

Although the adsorption of gases by charcoal has been measured at low temperatures, mainly in connection with the production of high vacua, little has been attempted along this line with catalytically active materials. Von Hemptinne[5] brought hydrogen, and in other experiments carbon monoxide, into equilibrium with platinum at $-78°$ and then allowed the system to warm gradually to room temperature. From observations of the pressure at a series of temperatures, he concluded that the gas adsorbed at low temperatures is gradually evolved on warming, until a temperature of about $-40°$ is reached, when a rapid increase in adsorption occurs. A similar phenomenon was observed with palladium and carbon monoxide. Nikitin[6] has recently reported adsorption measurements of hydrogen on nickel at three temperatures, -185, 19 and 336°, and finds that the adsorption is less at -185 than at 19°.

Experimental Method and Apparatus

Apparatus and Procedure.—The method of measuring the adsorption was the usual one which consists in a comparison of the volume of the gas required to fill a bulb con-

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[3] Gauger and Taylor, THIS JOURNAL, 45, 920 (1923).

[4] Terwen, *Chem. Weekblad,* 21, 386 (1924).

[5] Von Hemptinne, *Z. physik. Chem., 27,* 429 (1898).

[6] Nikitin, J. *Russ. Phys.-Chem. Soc., 58,* 1081 (1926).

taining the adsorbent at a given temperature and pressure, with the corresponding volume of an unadsorbed gas, in this case helium, which is required to fill the bulb at the same temperature and pressure. A number of measurements were made with an apparatus of the type now commonly used, which has been described by Pease.[7] To obtain more certain protection against the possibility of leaks at stopcocks, however, a modified type was constructed and employed for all experiments subsequent to Run 33.

The new apparatus, shown in Fig. 1, differs from the type used in earlier investigations in this Laboratory mainly in that all stopcocks exposed to vacuum are replaced with mercury seals. Pyrex glass is used throughout, and the capillary parts are of 1 mm. bore. The adsorption bulb A, of approximately 50 cc. capacity, communicates by capillary tubing with the mercury seal C which leads to the Töpler pump, with the closed manometer B of 6 mm. bore, and with the mercury seal E, of 16 mm. bore, the essential purpose of which is to obviate the necessity of maintaining the stopcock G under vacuum for long periods of time. The capillary at E, sloping slightly downward to the left, facilitates admission of gas from F without danger of mercury droplets being driven into the capillary D. H is a water-jacketed buret in which gas volumes are determined by measuring on the closed manometer I (6 mm. bore) the pressure exerted when the gas fills the buret to a mark on the 6-mm. tubing immediately below the water jacket. The volume readings have been corrected for the small but varying amounts of gas retained in the calibrated capillary F. The manometers and mercury seals are operated by applying air pressure or vacuum to the bulbs below them.

The procedure in determining an adsorption isotherm consists in successively admitting known amounts of gas from H through FED to the previously evacuated bulb and, after bringing the mercury levels to b and D, respectively, measuring in each case the pressure produced at equilibrium. Equilibrium was considered to be established when the pressure readings remained constant for fifteen to thirty minutes, but this supposition was frequently checked by approaching the equilibrium from higher as well as lower pressures. Between such a "run" and the succeeding one the adsorbent was evacuated for about two hours, at 200° in the case of the former of the two nickel samples employed, and at 250° for the second.

Materials.—Hydrogen was prepared by electrolysis of 15% sodium hydroxide between nickel electrodes and purified by passage in succession over heated platinized asbestos, soda-lime, calcium chloride and phosphorus pentoxide. Helium used in the free space determinations was purified by passage over heated copper and copper oxide and over active charcoal cooled with liquid air.

The nickel adsorbent was obtained by dehydrating c. p. crystalline nickel nitrate in a current of dry, carbon dioxide-free air at temperatures up to 400°, transferring the nickel oxide thus produced to the adsorption bulb, which was then sealed to the apparatus, and reducing in a stream of hydrogen for about twenty-four hours at each of the three temperatures 200, 250 and 300°. The two samples of nickel were prepared from the same batch of oxide, but reduction was stopped when the amount of water given off per hour was 2.5 mg. in the former case and 3.6 mg. in the second. The weights of metallic nickel were 23.68 and 23.10 g., respectively.

Constant Temperature Baths.—The temperature range covered by these measurements was 110 to −210°. For 110 and 56.5° toluene and acetone, respectively, boiling under atmospheric pressure, were used For temperatures from 0° down, Dewar flasks formed the bath containers: 0° was obtained with ice and water, −78.5° with solid carbon dioxide and alcohol. The intermediate temperature, −35°, was produced by periodically adding solid carbon dioxide to alcohol. For maintaining −183° liquid oxygen containing only a negligible quantity of nitrogen was employed, for −191.5°

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[7] Pease, THIS JOURNAL, 45, 1197 (1923).

liquid air, while for lower temperatures liquid air was allowed to boil under a pressure of a few cm. of mercury.

Considerable difficulty was experienced in obtaining satisfactory thermostats at temperatures between −78.5 and −183". For a temperature around −110° fair success was arrived at with a mixture of solid and liquid carbon disulfide, but it is difficult to maintain for long periods at the true melting-point (−111.6"). The solid carbon disulfide may be conveniently prepared by pouring the partially cooled liquid into liquid air, or vice versa. For temperatures between −160 and −170° the adsorption bulb was surrounded by a hollow cylinder, closed at top and bottom and constructed of 0.25-inch brass, which was wound externally with resistance wire, covered with alundum cement, and the whole immersed in liquid air. It was found that on passing a constant small current through the resistance wire, a fairly constant temperature could be maintained, and no temperature gradients could be detected inside the cylinder.

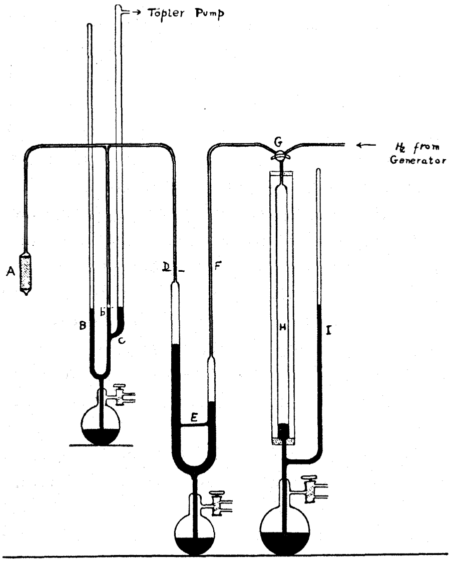

Fig. 1.—Apparatus.

Temperatures below 0° were determined with a copper-constantan thermocouple in connection with a Leeds and Northrup potentiometric temperature indicator. The couple was calibrated at 0, −78.5, −111.0 and −183°. Interpolation between these points and extrapolation below −183" were carried out with the help of a deviation curve prepared from the values given by Adams.[8] In spite of the fact that the deviations from Adams' values were very nearly a linear function of the observed e. m. f. down to −183°, continuation of the curve below this point led to a temperature of −193" for fresh liquid air, and temperatures below −200" determined in this way were obviously too low because in one experiment the calculated amount of free space exceeded the amount of gas actually in the bulb. For this reason the part of the calibration curve below −183° which we have adopted as most nearly correct, placing fresh liquid air at −191.5°, may be in error, but it is believed that this probably does not exceed ±0.5°.

Determination of Free Space.—The volume of the free space in the bulb and connecting tubing to the marks b and D, Fig. 1, was determined by filling with pure helium at each of the temperatures, 110, 0 and −78.5"; for the second adsorbent −109° was also used. Since it was feared small quantities of helium might be adsorbed at lower temperatures, the volume of gas required to fill the free space at these points was calculated by the use of the perfect gas law from each of the measurements at the higher temperatures, consideration being given to the fact that a small measured volume in the capillary tubing always remained at room temperature. The close agreement of the values calculated in this way from the various temperatures used experimentally indicates that helium is not appreciably adsorbed at the pressures employed at temperatures at least down to −109°.

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[8] Adams, "International Critical Tables," Vol. I, 1926, p. 58.

Experimental Results

Typical isotherms obtained at various temperatures are shown in Figs. 2–4. The ordinates represent volumes, in cc. at 0°, 760 mm., adsorbed by 23.68 g. of nickel in case of Sample I (Runs 1–23), or by 23.10 g. for Sample II (Runs 34–52); the abscissas are the corresponding pressures in cm. of mercury at 0°. It is impracticable to present in this form the results of the entire series of 42 runs. Of this number 13 were devoted to the determination of free spaces, and about half of the remainder were redeterminations of isotherms already obtained on one or the other sample. (Runs 24–33 are omitted since they were made for a different purpose.)

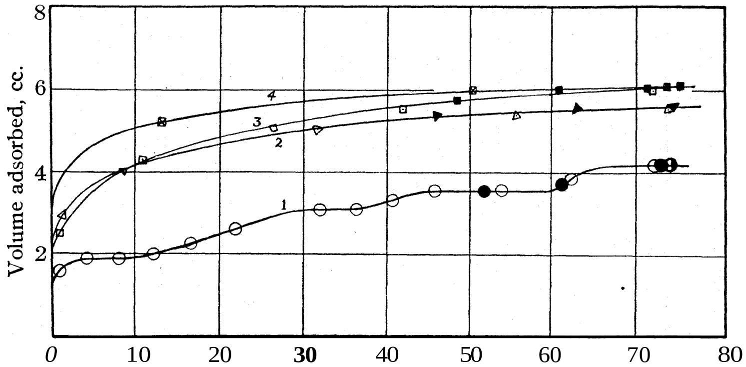

Fig. 2.—Adsorptions of hydrogen on nickel, Sample I. Curve I, −191.5° (Run 13); Curve 2, 56.5° (Run 15); Curve 3, 110° (Run 12); Curve 4, −35° (Run 16).

Reversibility with Respect to Pressure Changes.—In the majority of runs, after measurements had been made nearly up to atmospheric pressure, as large a portion of gas as practicable was withdrawn from the bulb and the course of the isotherm retraced to its upper end. In some cases this process was repeated several times. The values thus obtained are indicated in Figs. 2–4 by full black circles, triangles, etc. It will be observed that, while the exact equilibrium value was not always reached on first ascending the isotherm, nevertheless the values obtained from higher and from lower pressures agree so closely that the equilibrium isotherm can be drawn in every case with considerable confidence. This is especially true at the lower temperatures, where no evidence of hysteresis was ever observed. It is clear, therefore, that with respect to changes in pressure the adsorptions are strictly reversible.

Rate of Adsorption.—The rate of approach to equilibrium depended greatly on the experimental temperature and pressure. It is a remarkable fact that at −183 and −191.5° the pressure in the bulb became constant almost immediately after admitting the gas, whereas at both higher and lower temperatures considerably longer periods were required. It was also observed that in the higher temperature range equilibrium was reached less quickly at low pressures than at higher pressures. In the latter range times of the order of an hour were usually required, but as much as two hours was often necessary at pressures below 200–300 mm. However, at those points where the entire quantity of gas admitted to the bulb was adsorbed with a value of the final pressure practically equal to zero, shorter times were again required, of the order of half an hour.

Accuracy of Individual Isotherms.—The accuracy of any particular isotherm depends on the conditions employed. Volumes and pressures involve errors which are negligible in comparison with other factors. In those cases where the temperature remained definitely constant for long periods, as at −183, −78.5, 0, 56.5 and 110°, the limiting uncertainty is that involved in the exact establishment of equilibrium, amounting to not more than 0.1–0.2 cc. even at the higher temperatures. At the other temperatures, and particularly below −191.5° where the volume of gas in the free space is very large compared to the volume adsorbed, the limiting factor is the constancy and accuracy of the temperature. In these cases the temperature could be held constant within ±0.5°. Although the error in a single adsorption measurement produced by such a variation amounts to only 0.3 cc. at −110° and one atmosphere and proportionately less for lower pressures, nevertheless at −210° the uncertainty rises to nearly 2 cc.

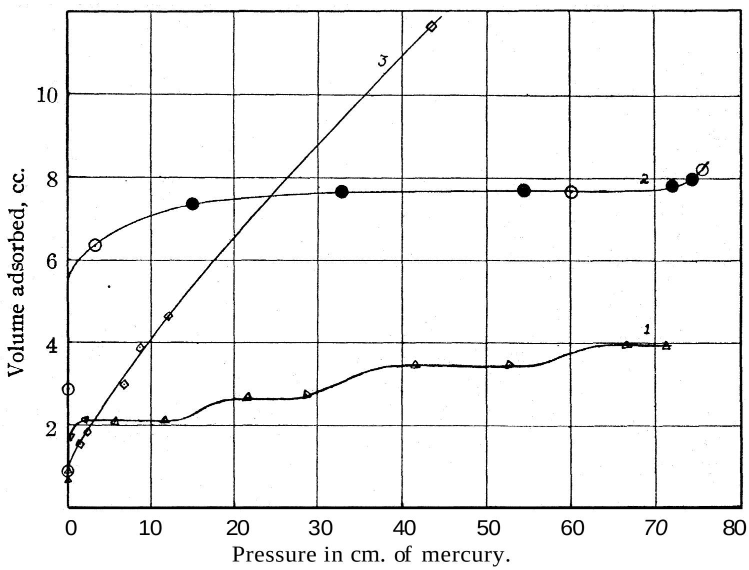

Fig. 3.—Adsorptions of hydrogen on nickel, Sample II. Curve 1, −191.5° (Run 39); Curve 2, −78.5° (Run 47); Curve 3, −209° (Run 49).

at atmospheric pressure. At this temperature there is an additional uncertainty, which is probably of even greater magnitude, in determining the absolute value of the temperature from the thermocouple calibration. For these reasons measurements below −200° must be regarded as fair approximations only, except at the lower pressures, yet the general trend of the true isotherms cannot differ greatly from those we have obtained. At all higher temperatures the accuracy is probably at least as great as that with which Figs. 2–4 can be read.

Comparison of Results for Different Temperatures.—In order to determine to what extent the values obtained for a given sample are reproducible, a large proportion of the runs (which are numbered serially in the order in which they were made) were devoted to checking earlier determinations. It was found that only a very small change in adsorption occurred in the case of Sample II. Thus the first run (34) and one near the end (50), both at 0°, gave exactly similar curves and differ only in the fact that in Run 50 about 0.3 cc. more hydrogen was adsorbed at all pressures than in Run 34. It is felt, therefore, that for this sample changes in activity with time are of the same order of magnitude as the probable error of the individual isotherms. Sample I, however, showed a steady and fairly considerable decrease in adsorptive capacity throughout, although here also only the absolute values were affected and not the shape of the isotherms. This change should be considered in comparing the curves of Fig. 2. While sufficient data have been obtained to correct systematically for this variation, it appears unnecessary to do so, since all the temperatures at which Sample I was investigated were also used with Sample II, except —35, 56.5 and 110°.

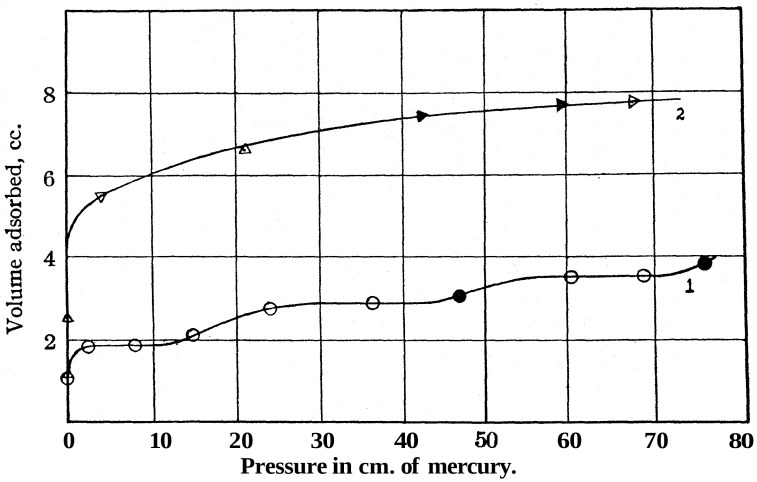

Fig. 4.—Adsorptions of hydrogen on nickel, Sample II. Curve 1, −183° (Run 52); Curve 2, 0° (Run 50).

In order to make the values for Sample I at these temperatures suitable for comparison with the data at other temperatures for Sample II, we have assumed that the ratio of the adsorptions at two temperatures is the same for each sample. This is closely the case for temperatures at which both samples were actually studied. Since several runs at 0° were made at wide intervals on each sample, this is a convenient temperature at which to make the comparison. The method will be clear from the following example. At 110° and 600 mm. pressure 7.77 cc. was adsorbed in Run 6 and 5.85 cc. in Run 12. At 0° and 600 mm. the adsorptions were 6.93 cc. in Run 11 and 6.25 cc. in Run 14. Hence at this time the decrease in adsorption amounted to about 0.3 cc. per run at this pressure. If Run 12 could have been made at the same time as Run 14, we should expect, therefore, that 5.85 − 0.6 = 5.25 cc. would have been adsorbed. Hence for Sample I the corrected value for 110° is 5.25/6.25 times the value at 0°. If we assume that this same ratio holds for Sample II, which in Run 50 took up 7.70 cc. at 0° and 600 mm., the adsorption at 110° and 600 mm. would be 5.25/6.25 X 7.70 = 6.49 cc.

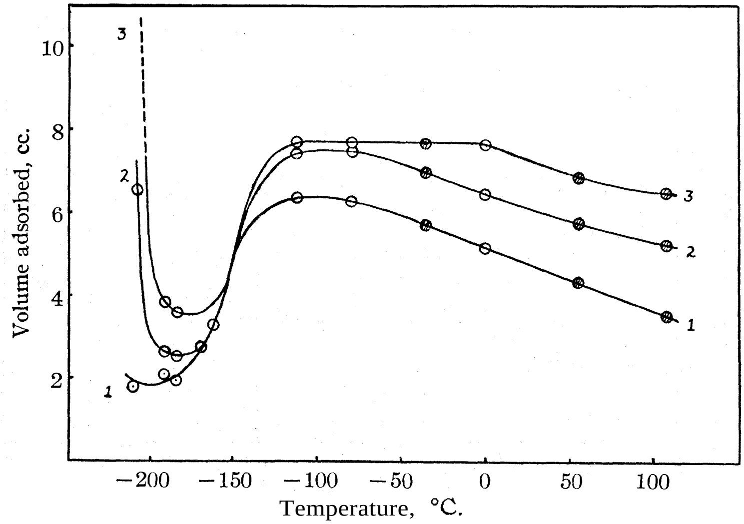

Fig. 5.—Isobars for hydrogen on nickel: Curve 1, at 2.5 cm. pressure; Curve 2, 20 cm.; Curve 3, 60 cm.

Similar calculations have been made for 25, 200 and 600 mm. pressure at the three temperatures —35, 56.5 and 110°. The values so obtained, together with those interpolated from the experimental isotherms for Sample II, are included in Fig. 5, in which the ordinates represent volumes adsorbed and the abscissas temperature, and the three curves are the isobars for 25, 200 and 600 mm., respectively.

Test of Reversibility with Respect to Temperature Change.—At the conclusion of the experiments described above, a working hypothesis to account for the observed variation of adsorption with temperature led us to an attempt to follow the equilibrium from higher to lower temperatures without intervening evacuation. In a run made at 0° in the regular way 7.40 cc. of hydrogen was adsorbed at a pressure of 631.4 mm. Without altering the amount of gas in the bulb the latter was then cooled to liquid air temperature. After apparent equilibrium had been reached, it was found that 9.85 cc. was now adsorbed at a pressure of 184.1 mm., whereas in a run (Run 39, Fig. 4) in which the gas was directly admitted to the bulb at this temperature, only 2.5 cc. was taken up at 184.1 mm. The same gas was then allowed to remain in contact with the nickel at room temperature for twenty-one hours. Following this, a remeasurement at 0° showed 8.22 cc. adsorbed at 636.2 mm., the increase over the previous value at 0° probably being due to a very slow solubility of hydrogen in the nickel. On cooling to $-186°$ the pressure became constant at 189.8 mm., at which 10.50 cc. was taken up. This increase of adsorption on cooling, 2.28 cc., agrees fairly well with the 2.45 cc. found in the previous part of the experiment. Subsequently additional gas was admitted to the bulb at $-186°$ and then withdrawn in stages. The following adsorptions were found: at 359.9 mm., 10.47 cc.; at 148.2 mm., 10.06 cc.; at 74.2 mm., 9.72 cc.

These results show that, contrary to what would be expected from a consideration of the individual isotherms, hydrogen adsorbed at 0° is not evolved on cooling to $-190°$, at least at an appreciable rate, but instead an increased adsorption occurs. This increase, 2.45 cc. and 2.28 cc. in the two trials, is of the same order of magnitude as the entire adsorption found at $-191°$ when the gas is admitted directly at this temperature. These facts strongly suggest that hydrogen can be adsorbed by nickel in two different ways, a strong binding being characteristic of the higher temperature range and a looser binding at low temperatures. The rate of change of the adsorbed gas from one form to the other is inappreciable at low temperatures.[9] For this reason either the low-temperature isotherms directly determined, or the values obtained after cooling from 0°, or perhaps both, represent metastable equilibria. It appears that the only hope of determining experimentally the values which correspond to true thermodynamic equilibrium at temperatures below $-110°$ lies in greatly extending the times of observation.

However, the fact that the isotherms are completely and quickly reversible with respect to pressure changes indicates that the metastable states are perfectly definite and in no sense mere accidental stopping-places on the

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[9] More recently we have found that the equilibrium, which is almost immediately established at $-183°$ when hydrogen is directly admitted at this temperature, remains unchanged for at least seventy hours.

way to true equilibrium. In this respect the situation appears to be analogous to the numerous cases of chemical reactions, such as the addition of hydrogen to benzene to form cyclohexane, where the reactants and products quickly reach a definite equilibrium of undoubted significance in spite of the fact that one or more of the reacting substances is itself unstable with respect to other possible reactions.

Discussion

The major results of this investigation can readily be accounted for on the hypothesis that at the lowest temperatures the adsorption is of the secondary type, involving hydrogen molecules whose configuration is little if at all altered by the process, whereas at temperatures above −100° only primary adsorption occurs, in which the adsorbed molecules suffer a marked activation and perhaps even complete dissociation. The flatness of the 60-cm. isobar from −110 to 0° is strongly suggestive of the idea that here the nickel surface is entirely saturated with a single layer of these activated molecules. At temperatures above 0°, pressures higher than 60 cm. would evidently be necessary to complete the layer. On this view the additional hydrogen which is taken up at low temperatures after the nickel has been saturated at 0° corresponds to the partial formation of **a** second layer. The isothermal results at temperatures below −191° suggest that at still lower temperatures multimolecular layers are also capable of existence.

Between −100 and −191° the adsorption appears to consist of both types. It is obvious, however, that in this range the observed values cannot be accounted for on the basis of an equilibrium between the two types since the experiments described in the last section show that the rate at which this equilibrium is established is negligibly small. For the same reason it is impossible to consider that the results in this region represent a continuous variation in the degree of activation of the adsorbed molecules. It must be supposed that primary and secondary adsorption constitute, at least in the present example, separate and distinct types, and not merely limiting cases of a continuously variable property. (It is not meant to be implied, however, that all the hydrogen held by primary adsorption necessarily has the same chemical reactivity.) We believe that the values obtained in this intermediate range are best explained by assuming that, as the temperature is raised, a larger and larger fraction of the nickel surface is capable of producing activation in the adsorbed molecules. At the same time the secondary adsorption, which falls off much more rapidly with decreasing pressure than the primary, is continuously decreasing. The opposition of these two effects results in a minimum in the isobars, which lies at temperatures which are lower the lower the pressure.

The isotherms for temperatures above −110° show nothing unexpected except that above 0° they are considerably less flat than those obtained by

Gauger and Taylor.[3] As the temperature is raised in this region, higher and higher pressures are required to produce saturation of the surface, and a progressive change in the shape of the isotherms occurs. The curves for temperatures below −200° are typical of adsorption without activation, except that about 1 cc. of gas is adsorbed at zero pressure, a fact which presumably indicates that even at these temperatures nearly one-eighth of the surface is capable of activating the hydrogen.

The isotherms obtained at −183 and −191° warrant special mention. Owing to the almost instantaneous establishment of equilibrium and the extreme constancy of the temperature at these points, the individual values found here are probably more precise than at any other temperature. Nevertheless, smooth curves cannot be drawn through the experimental points within the limit of accidental error, which probably does not exceed 0.05 cc. Systematic errors, such as would result from deviations from the gas laws or uncertainty in determining the absolute temperature, could not account for the observed behavior. Furthermore, the anomaly is found in every isotherm at these temperatures, and only at these temperatures. For these reasons it appears that the stepwise increase of adsorption with pressure must have some physical significance. It should be pointed out, however, that the data obtained are insufficient to locate the exact course of the curves between steps, a point which is still under investigation.

The following tentative interpretation of this phenomenon may be proposed. At either temperature a fraction of the adsorbing surface, equivalent to about 1.5–2.0 cc. of gas, holds hydrogen by primary adsorption to an extent practically independent of pressure. On top of this and on the remainder of the surface, adsorption of the secondary type occurs, as indicated by its reversibility, which experiment shows does not occur at these temperatures for the primary type. It appears also that the surface is a composite one, which may perhaps be thought of as presenting a number of distinct regions of different adsorptive capacity. On each of these regions the adsorption represents an equilibrium between condensation and evaporation. If it be assumed that the rate of evaporation is very great for isolated molecules but much less when a number are adsorbed side by side, it follows that scarcely any adsorption would occur on a given region until the pressure reached a point at which the rate of condensation was sufficiently high to produce patches of neighboring adsorbed molecules. At this point further increase of pressure would quickly lead to the formation of a saturated layer. It appears that a summation of such effects on the different regions of the surface would result in an isotherm of the form found experimentally.

Summary

The adsorption of hydrogen by two samples of reduced nickel has been studied at pressures from zero to one atmosphere and at eleven tempera-

tures from 110 to $-210°$. The apparatus employed involves no stopcocks that are required to remain under vacuum more than momentarily.

At a given pressure the adsorption is relatively large at the lowest temperatures, decreases to a minimum at -200 to $-175°$ depending on the pressure, then rises to a maximum in the neighborhood of $-100°$, and finally decreases again at higher temperatures. The fact that at 600 mm. the adsorption is independent of the temperature from -110 to $0°$ is taken as evidence that here a completely saturated single layer is formed.

It is shown that the values obtained are reproducible, and readily reversible with respect to changes of pressure, particularly at the lower temperatures. However, on cooling to about $-190°$ a sample previously brought to equilibrium at $0°$, the adsorption does not decrease to the value obtained isothermally at $-190°$, but reaches a new reversible equilibrium at which larger quantities of gas are adsorbed than at $0°$.

At -191 and $-183°$ the adsorption increases with pressure in a discontinuous manner, an observation whose explanation is somewhat obscure.

The major results of the work are interpreted on the hypothesis that at the lowest temperatures the adsorption is of the "secondary," or ordinary molecular type, while at higher temperatures a progressively larger fraction of the nickel surface is capable of holding the hydrogen by adsorption of the "primary" type, involving a marked activation of the gas.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

THE INCOMPATIBILITY BETWEEN ANY THEORY OF COMPLETE DISSOCIATION AND MIGRATION DATA

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Inspection of the migration data for solutions of pure single electrolytes cannot, in general, give very conclusive evidence for or against the existence of any but the simplest ions in such solutions. In general, migration ratios are not constant throughout a range of concentrations, but it is a matter of rather arbitrary interpretation as to whether this is due to the ions being unequally affected by increase of concentration or whether the appearance of new (complex or intermediate) ions is assumed to account for the change in the gross transport number. It is only in the few rare instances, such as the well-known case of cadmium iodide where the change in transport number becomes so great that the sign of the migration is actually changed, that this method yields any conclusive proof of the existence or presence of complex ions.

It is evident that, if the migration number of a salt such as potassium chloride changes somewhat upon concentration, the change would most readily be ascribed to unequal change in the mobilities of the K^+ and Cl^- ions, whichever of the various explanations for such behavior might be adopted. The same would be true for the case of such a salt as sodium chloride, the constitution of whose solution might be expected to be very similar to that of potassium chloride. Moreover, a point which has escaped adequate appreciation, the same would be true of an examination of the movement of the common ion such as the chloride ion in a mixture of sodium and potassium chlorides. The results would be just as inconclusive as if either salt alone had been employed. The measurements of MacInnes[1] and Miss Dewey[2] are, therefore, necessarily inconclusive.

It is otherwise when the two salts are mixed in very unequal proportions, and the movement of the cation present in smaller quantity is directly measured. Here the excess of the salt present in larger proportion has the effect of largely increasing the relative concentration of any complex ions which can be formed from the lesser constituent, and, if so, the migration of the single dilute ion is greatly affected.

In our previous communication[3] we took advantage of this circunistance to test for the presence of complex ions in mixtures of such salts as magnesium and ammonium sulfates or magnesium and ammonium chlorides. For example, in a mixture of 0.05 M $MgSO_4$ with 0.93 M K_2SO_4 the magnesium actually migrates in the direction of the anode instead of going toward the cathode. This affords the most unequivocal proof possible that a negative charge appertains to most of the magnesium present. In other words, there is more transport of magnesium in negatively charged form (complex anion) than there is of ordinary magnesium ion itself. This negative movement of the material of the dilute ion (ignoring the movement of the concentrated cation or the common anion) serves, therefore, as a remarkable and trustworthy indicator for the presence of complex ions in considerable amounts in those mixtures.

Hence we must further conclude that in a solution of one of the salts

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[1] D. A. MacInnes, THIS JOURNAL, 47, 1922 (1925); D. A. MacInnes, I. A. Cowperthwaite and T. Shedlovsky, *ibid*, **51**, 2671 (1929). In this connection it may be noted that MacInnes' formula appears to contain an assumption which renders it not strictly applicable to mixtures above a total concentration of 0.2 equivalent per liter, such as the higher concentrations studied by Schneider and Braley, *ibid.*, ***45***, 1121 (1923). Moreover, this formula presupposes that potassium and sodium chlorides are dissociated to the same extent, an assumption which, for example, is rejected by Nernst [*Z. physik.* **Chem., 135,** 237 (1928); Orthmann, ***Ergebnisse der exakten Naturwiss., 6,*** 189 (1927)].

[2] J. Dewey, THIS JOURNAL, 47, 1931 (1925).

[3] J. W. McBain and P. J. Van Rysselberge, *ibid.*, 50, 3009 (1928). Through inadvertence, the total amount of current passed was omitted from Table I. The coulometer readings in grams of silver deposited were, in order of the experiments listed: 0.22205, 0.16945, 1.48005, not measured, 0.3853, 0.72065, 0 03975, 1 7300, 1 0212, 0.9476, 1.0318, 1.8467, 1.7912, 0.8277, 0 7202.

alone, if complex ions are present in these mixtures in such significant amounts that they overshadow the ordinary migration of the dilute ion, we have to recognize the presence of such complexes in the solutions of the corresponding single electrolytes of the same total concentration as the mixture. Indeed, as is evident from the principle of mass action, the concentration of the complexes will be even greater in absolute amount, but, of course, the proportion relative to the total concentration is correspondingly lowered and the considerations deduced in the first two paragraphs will apply. What such measurements of transport in mixed solutions achieve is, therefore, to prove the existence of important amounts of complex ions, and that only if the migration of the single dilute ion is actually measured. Evaluation of the exact amounts of the complexes present requires the combination of supplementary methods, such as determinations of e. m. f. of the single constituents and total freezing-point lowering, conductivity, etc.[4]

The measurements communicated in the previous paper showed that the formation of complex ions is general throughout all solutions containing polyvalent ions. This, of course, would render futile any attempt to apply hypotheses of complete dissociation to solutions containing such ions save in extreme dilution, where all theories agree in assuming complete dissociation. The complex ions are probably formed by combination of ordinary undissociated molecules with ions. Mere clustering of ions through the operation of electrostatic forces (Bjerrum's term "association") appeared inadequate as an explanation of the migration effects observed, because it should result in comparable amounts of complex cations and anions being formed and leave the migration essentially unaffected.[5] Hence the results point not only to the presence of complex ions but to ordinary undissociated molecules as well. Hydration of ions as ordinarily recognized is quite inadequate to explain away these results.

The present investigation shows that the negative migration of magnesium in a mixture of magnesium sulfate with the sulfate of one of the

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[4] We have attempted such a complete evaluation for solutions of cadmium iodide and cadmium sulfate, to be published elsewhere.

[5] An experiment was carried out on the movement of chlorine in the mixture **0.05 M $MgCl_2$ + 1.95** M $MgSO_4$. For a total current corresponding to **0.4631** g. of silver, the changes observed were: middle, +0.6%; cathode, **0.968** mg. Calculated by the usual approximation of the isohydric principle, the migration of the chlorine in the magnesium chloride is **0.95,** which is about what would be expected for a highly concentrated solution of magnesium chloride. Its chief significance is to show that there is no anomalous movement toward the cathode, whereas in all the other mixtures that have common anion instead of common cation there is a large movement of the dilute ion toward the "wrong" electrode. Hence we arrive at the important result that the effects are not symmetrical; complex anions have to be assumed in large amount, but not complex cations. This does not accord with purely physical explanations.

least hydrated ions, rubidium, is just as pronounced as before. The measurements are also extended to solutions containing only univalent ions such as mixtures of sodium and potassium chlorides.

Experimental

The migration apparatus was that used in the previous work[3] except for the chloride experiments.[6] The current of average strength, 0.05 ampere, was measured in a silver coulometer. The electrodes were of platinum except in the case of the mixture of sulfates when a copper anode was used. The solution, whose weight and composition by volume were known, was introduced into the cleaned and weighed apparatus. After the experiment about 50 cc. was withdrawn from the middle portion; 11 cc. was locked in the tap and served as a second middle portion. The anode and cathode portions were then closed with rubber stoppers and weighed. The weights of the solution in the two portions were thus known. In most experiments samples were then taken from the anode, cathode, middle and original solutions, weighed in weighed pyrex beakers and analyzed. The experiments were carried out at room temperature.

Magnesium was estimated as phosphate after precipitation with ammonium phosphate. In the first recorded experiment the precipitates obtained by the phosphate method were much heavier than expected from the composition of the pyrophosphate and the concentration of the solution. It was found that these precipitates contained rubidium, their probable formula being $3P_2O_5{\cdot}4MgO{\cdot}2Rb_2O$. In the second experiment carried out on the same mixture, the first precipitates were dissolved in hot hydrochloric acid and then reprecipitated. The usual ammonium magnesium phosphate was obtained.

Rubidium was precipitated and weighed as rubidium sodium cobalt nitrite. Analysis of the anode portions, however, gave irregular results, probably due to the presence of copper from the anode, so that the cathode results alone are recorded.

The transference numbers are calculated as in the previous paper on the approximate assumption that the current is distributed between the two constituents of the mixture in proportion to their respective concentrations and to the specific conductivities of the salts separately in concentrations equal to the total concentration of the mixture. The total current is indicated in the second column of the tables in terms of the silver deposited in the coulometers.

TABLE I

MIGRATION DATA IN MIXTURES OF RUBIDIUM AND MAGNESIUM SULFATES, SHOWING THAT EITHER MAGNESIUM OR RUBIDIUM IN THE PRESENCE OF EXCESS OF THE OTHER SULFATE MIGRATES TO THE ANODE

Concn. of mixture, moles per liter	Ag, g.	Change			Observed migration
		Middle, %	Cathode, mg.	Anode, mg.	
0.05 $MgSO_4$ + 0.95 Rb_2SO_4	0.3113		Mg negative		
0.05 $MgSO_4$ + 0.95 Rb_2SO_4	.3867	0.02		+0.00128	−1.87 −0.65
0.025 Rb_2SO_4 + 1.975 $MgSO_4$	(.9118)	2	−0.0082		− .19
0.025 Rb_2SO_4 + 1.975 $MgSO_4$	.619	0.1	− .0038		− .13
0 025 Rb_2SO_4 + 1.975 $MgSO_4$	(.9719)		Rb negative		

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[6] J. W. McBain and R. C. Bowden, J. *Chem. Soc.*, 123,2417 (1923).

Mixtures of Ammonium and Potassium Iodide

Potassium iodide containing 2% equivalent ammonium iodide was chosen because of the convenient analytical method for the determination of the (NH_4) constituent. The solution is neutralized, then treated with excess of neutral, filtered formaldehyde. The ammonium salt is quantitatively decomposed, forming hexamethylenetetramine with the formation of an equivalent amount of hydriodic acid, which is directly estimated by titration. The systematic error of 2% in this method does not affect the conclusions, since the results are all obtained by difference. However, at times the reaction appears more complicated, probably due to hydrolysis or reactions at the electrodes, for duplicated points were sometimes not reproducible. Even so, though irregular, the results show qualitatively that the transference of the ammonium constituent is decreased or almost suppressed by the presence of a large excess of iodine ions due to complexes containing NH_4^+ ion. Iodine was liberated at the anode and formed a solution which diffused in the whole anode portion and to a slight extent in the middle portion. Four samples were taken of each portion, cathode, middle and anode, and directly compared with the original solution. Table II contains the migration data for the mixtures of ammonium and potassium iodides of total concentration from 0.5 to 2.0 equivalents per liter.

TABLE II

MIGRATION DATA POR MIXTURES OF POTASSIUM AND AMMONIUM IODIDES, SHOWING THAT MOVEMENT OP AMMONIUM IS LARGELY SUPPRESSED BY EXCESS OF POTASSIUM IODIDE[a].

Concn. of mixture, moles per liter	Ag, g.	Change in NH_4 content Middle, %	Cathode, mg.	Anode, mg.	Migration, n_{NH_4}
0.1 NH_4I	0.1730	...	+14.46	− 7.96	+0.501
1 NH_4I	.1330	−0.9	+10.42	−11.23	+ .531
.01 NH_4I + 0.49 KI	.4043	+ .4	.....	− 0.16	+ .11
.012 NH_4I + .588 KI	.3490	+ .7	+ 0.3	− .31	+ .26
.015 NH_4I + .735 KI	.5860	+ .1	+ .38	− .45	+ .21
.016 NH_4I + .784 KI	.5980	+ .2	+ .09	− .28	+ .14
.018 NH_4I + .882 KI	.3953	+ .66	.00	.00	.00[b]
.02 NH_4I + .98 KI	.3930	+ .3	.....	− .04	+ .03
.04 NH_4I + 1.96 KI	.5650	+ .5	.....	.11	+ .06

[a] Other experiments by Mrs. M. E. McBain (née M. E. Laing) showed a decreased migration number of the same order of magnitude. 0.01 NH_4I + 0.49 KI gave a transport number of +0.4, and 0.02 NH_4I + 0.98 KI gave transport numbers of +0.17 and +0.13 (instead of 0.5). [b] The change in the middle portion is greater than the change in the anode and cathode portions.

Mixtures of Potassium and Sodium Chlorides

The experiments of others on mixtures of chlorides have already been referred to, but it is to be noted further that all their work has been carried out with a ratio of the two salts under 4 to 1 and a total concentration of chiefly 0.1 or 0.2 N, respectively. The ratios of sodium to potassium in this work are 49, 24 or 9, to 1, the total concentration being either 2.0 or 5.0 N. The data refer to the movement of the potassium.

The apparatus used in these experiments consisted of three U-tubes connected by ground joints. These tubes were provided with ground stoppers which allowed an easy removal of three middle portions; namely, a central middle portion, an anode middle portion and a cathode middle portion, the two latter being contained in the horizontal tubes connecting the U-tubes. Both anode and cathode were made of platinum.

Potassium was precipitated and weighed as sodium potassium cobalt nitrite. It was found that potassium may be precipitated from these solutions in many different forms, corresponding to different degrees of hydration of the complex nitrite. It was also found that the composition of the precipitate increases with the time of settling, probably on account of gradual hydration. In order to obtain directly comparable results, it is necessary to carry out all the analyses under strictly identical conditions: the total volumes of the samples before precipitation must be the same; the same amount of sodium cobalt nitrite must be added to each of them; the time of settling must be the same for all the samples and should be at least twelve hours; the washing and drying of the precipitates should be carried out under constant conditions. In spite of all these precautions, a difference of about 1.3% is sometimes found between samples which should give identical weights of precipitates. This seems to be due to a difference in composition corresponding to one-third of a molecule of water.

TABLE III

MIGRATION DATA FOR MIXTURES OF POTASSIUM AND SODIUM CHLORIDES, SHOWING THAT THE MIGRATION NUMBER OF POTASSIUM CHLORIDE IS GREATLY ALTERED BY PRESENCE OF EXCESS OF SODIUM CHLORIDE

Concn. of mixture, moles per liter	Ratio, $\frac{NaCl}{KCl}$	Ag, g.	Change in K content			Migration,[a] n_K
			Middle, %	Cathode, mg.	Anode, mg.	
0 2 KCl + 1.8 NaCl	9	0.7121	<0.4	+14.39 +15.90	−14.71 −12.45	+0.407
.08 KCl + 1.92 NaCl	24	.6963	<.2	+ 5.68 + 4.59 + 6.35	− 4.31 − 4.34	+ .352
.04 KCl + 1.96 NaCl	49	.8922	...	+ 3.20 + 3.73	− 2.71	+ .352
.5 KCl + 4.5 NaCl	9	1.3479	<.2	f31 13 +30.98	−18.02 −22.62	+ .287
.2 KCl + 4.8 NaCl	24	1.6336	<.3	+17.65 +19.85 +14 47	− 8.52	+ .344

[a] The values of the transport number of potassium given in Table III are those calculated from the observed data according to the isohydric principle; they should be compared with that for potassium chloride alone, namely, 0.5.

The changes in content of potassium at the electrodes are calculated by comparing the amounts of complex nitrite given by weighed samples with the amounts of complex given by weighed samples of the original solution.

Nernst's recent modification of the theory of strong electrolytes leads to unequal degrees of dissociation for potassium and sodium chlorides, sodium chloride being more dissociated than potassium chloride. Nernst's theory affords values for the degrees of dissociation, and it was found that these degrees of dissociation obey the law of mass action.

It is interesting to see if the low values found for the movement of potassium cannot be accounted for by the decrease of the degree of dissociation of potassium chloride, due to the presence of the large amount of sodium chloride. Table IV gives the values of the (Nernst) degrees of dissociation of potassium and sodium chlorides for the concentrations used in our experiments. In the calculations it has been assumed that the dissociation of sodium chloride is not affected by the presence of the small amount of potassium chloride. The modified values of the degree of dissociation of potassium chloride, combined with the fractions of the current carried by potassium chloride on the assumption that the two salts are independent of each other, allow us to predict the transport number of potassium. It can be seen in Table IV that the predicted and measured values agree quite well.

TABLE IV

COMPARISON OF OUR OBSERVED DATA WITH THOSE PREDICTED FROM THE NERNST FORM OF THE DISSOCIATION THEORY

Concn. of mixture, moles per liter	Degree of dissociation of KCl in pure solution	KCl in mixture	NaCl	Predicted migration	Measured migration
0.2 KCl + 1 8 NaCl	0.950	0.700	0.834	0.357	0.366
0.08 KCl + 1.92 NaCl	.998	.625	.825	.308	.294
0.04 KCl + 1.96 NaCl	1.000	.605	.827	.299	.281
0.5 KCl + 4.5 NaCl	0.890	.526	.704	.287	.265
0.2 KCl + 4.8 NaCl	.950	.525	.694	.268	.268

It remains an open question whether the decrease in the degree of dissociation of potassium chloride, due to the presence of the large excess of sodium chloride, is the real explanation for the low values found for the movement of potassium or whether the agreement between the predictions of Nernst's theory and our experimental values is the result of a mere coincidence, complex ion formation having been neglected.

Mixtures of Potassium and Sodium Nitrates

One experiment was carried out on the following mixture: 0.08 N KNO_3 + 1.92 N $NaNO_3$, and the same procedure as for the mixtures of potassium chlorides was followed. Table V gives the results of this experiment.

The degrees of dissociation of pure 0.08 N KNO_3 and of pure 1.92 *N*

TABLE V

MIGRATION DATA SHOWING THAT PRESENCE OF SODIUM NITRATE LOWERS THE MIGRATION NUMBER OF POTASSIUM IN POTASSIUM NITRATE

Concn. of mixture, moles per liter	Ratio, $\frac{NaNO_3}{KNO_3}$	Ag, g.	Middle, %	Cathode, mg.	Anode, mg.	Migration n_K[a]
				+7.08		
0.08 KNO_3 + 1.92 $NaNO_3$	24	0.9678	<0.7	+8.87	−5.26	+0.396
				+7.69	−6.27	

[a] This number is that calculated on the assumption that the amount of current carried by the potassium nitrate is that calculated on the isohydric principle; it should be compared with that for pure potassium nitrate, namely, 0.613.

$NaNO_3$, according to Nernst,[7] are 96.4 and 69.9%, respectively. In the mixture, the degree of dissociation of potassium nitrate should, therefore, be 0.562. The movement of potassium should then be 0.5 X (0.562/0.964) or 0.292, when, in the calculation of the amount of current carried by potassium nitrate, the salts are considered as independent. The corresponding experimental value is 0.270.

Discussion

The migration data in Tables I–V, like those in our previous communication, show that in the majority of cases the presence of a large excess of anion reduces, suppresses or even reverses the movement of the supposed cation of a dilute solution of a strong electrolyte. These results are evidently incompatible with any assumption of complete dissociation into simple, independent ions.

Whenever the movement is reversed, more of the metal studied is being carried toward the anode than is migrating as simple ion toward the cathode. This is definite proof of the existence of complex anions, and in relatively large amount. For the reasons adduced in the previous communication these complex anions must be regarded as being formed by chemical combination of the ions with undissociated molecules present in the solution. The proportion of complex ions should increase rapidly with the concentration of the simple common anion of the mixture and, therefore, should also depend upon the degree of dissociation of the salt added in excess. Thus the addition of an ammonium or an alkali metal sulfate should cause a much greater change in migration number of a given salt than addition of such salts as copper or cadmium sulfates, as is illustrated by the experimental data. Furthermore, divalent ions show a larger tendency to complex formation than do monovalent ions.

Taking first the experiments of Table I for mixtures of sulfates, we see that excess of rubidium sulfate drives magnesium to the anode, whilst excess of magnesium drives rubidium to the anode. This shows that both magnesium sulfate and rubidium sulfate contain complex anions. The

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[7] See Orthmann, *Ergebnisse der exakten Naturwiss.*, 6, 193 (1927).

simplest assumption is that they are represented by the formulas $Mg(SO_4)_2^{=}$ and $Rb(SO_4)^{-}$, respectively, the latter being analogous to the HSO_4^{-} ion of sulfuric acid, which was usually held responsible for the formation of persulfuric acid in electrolysis. It is clear from these and all the other data so far available that divalent ions much more readily form complex ions than do monovalent ions.

Rubidium sulfate was chosen for study because the rubidium ion is recognized to be nearly anhydrous so that it is incapable of displacing large amounts of solution toward the anode by carrying along with it corresponding amounts of water toward the cathode. Hence the effect cannot be explained away as being due to hydration of the cation present in excess.

The numerical values of the migrations in these mixtures possess only semi-quantitative significance owing to the mode of calculation from the actual movements observed. Quantitative evaluation would require a knowledge of the formulas and actual mobilities of each of the ions present in the mixture, and the greater the formation of complex ions the more would such a result depart from the rule of simple mixtures on the principle of isohydrism. This may account for such an extreme number as -1.57, but the possibility of still higher complexes has to be borne in mind.

It may be worth noting here that C. W. Davies[8] has shown that the change in conductivity of magnesium sulfate with change in concentration is incompatible with the assumption of the complete dissociation of magnesium sulfate into single ions. Onsager's[9] conductivity equation, based on the hypothesis of 100% dissociation, fails completely for magnesium and cadmium sulfates, and Davies modified the equation by taking the incomplete dissociation into consideration.

Complex anions containing copper have been detected by Rieger[10] in solutions of the double sulfate $K_2Cu(SO_4)_2$. He found that here the migration of the copper ion was much smaller than in solutions of pure copper sulfate of the same concentration and that the transference number decreases when the concentration of the double sulfate increases. This is due presumably to the presence of complex anions, $Cu(SO_4)_2^{=}$, analogous to $Mg(SO_4)_2^{=}$.

Pfanhauser[11] found that in a saturated solution of nickel ammonium sulfate, the nickel moves entirely to the anode in the form of the complex ion $Ni(SO_4)_2^{=}$. Some incomplete data relating to a 0.1 molar solution of the double sulfate show that, even at this low concentration, the nickel is largely in the form of complex ions.

Tables II and III are especially interesting in that only uni-univalent

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[8] C. W. Davies, *Trans. Faraday Soc.*, 23, 351 (1927).

[9] L. Onsager, *ibid.*, 23, 341 (1927).

[10] E. Rieger, *Z. Elektrochem.*, 7, 863, 871 (1901).

[11] W. Pfanhauser, *ibid.*, 7, 698 (1901).

salts are concerned. Table III refers to potassium chloride, the typical strong electrolyte. The experiments show that the presence of a large excess of Cl^- can decrease the transference of potassium ion to about 55% of its value in a solution of potassium chloride alone. Similarly, excess of potassium iodide practically suppresses the movement of ammonium ion toward the cathode. Nernst's form of the dissociation theory would predict that the transference number of potassium chloride should tend toward a definite limit as the excess of sodium chloride present is increased. It is easily shown that the relative hydrations of sodium and chlorine ion as measured in such investigations as those of Washburn[12] and Miss Taylor and Sawyer[13] could not account for more than a very small fraction of the effects here observed.

Familiar examples of complex anions derived from uni-univalent salts are the $Ag(CN)_2^=$ of double cyanides and the mixtures[10] of potassium and silver iodides in which the silver likewise migrates toward the anode.

Measurements of activity coefficients in mixtures of electrolytes afford at least qualitative information as to the possibility of incomplete dissociation. Results obtained for hydrochloric acid in presence of alkali chlorides, such as those of Harned,[14] recalculated by Lewis and Randall,[15] show that in concentrated solutions "the activity coefficient of the hydrochloric acid depends upon the specific nature of the added chloride." This would indicate that a complete dissociation does not hold in these mixtures. The results obtained by Loomis, Essex and Meacham[16] with 0.1 molar mixtures of potassium chloride and hydrochloric acid are not exactly constant when the ratio of the concentrations of the two constituents varies. In general, if Lewis and Randall's ionic strength principle can be considered as closely verified for moderate concentrations, the deviations occurring at high concentrations can be accounted for by recognizing incomplete dissociation and, at least in the case of polyvalent salts, by taking into account the existence of complex ions.

Bronsted has published two experimental papers on electromotive force[17] which are most frequently quoted in support of the hypothesis of 100% dissociation. The first paper deals with cadmium electrodes dipping into two solutions containing two different concentrations of cadmium sulfate, the total concentration in each case, however, being made up to 2.0 molar by addition of magnesium sulfate. The electromotive forces were in substantial agreement with those calculated by using the gross concentration

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[12] E. W. Washburn, THIS JOURNAL, 31,322 (1909).

[13] M. Taylor and E W. Sawyer, J. *Chem. Soc.*, 2095 (1929).

[14] H. S. Harned, THIS JOURNAL, 42, 1808 (1920).

[15] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," The McGraw-Hill Book Co., New York, 1923, p. 367.

[16] N. E. Loomis, J. L. Essex and M. R. Meacham, THIS JOURNAL, 39, 1133 (1917).

[17] J. N. Brönsted, *Medd. Vetenskapsakad. Nobelinst.*, 5, No. 25, 1 (1819).

of cadmium sulfate in the usual Nernst formula. His very doubtfully valid procedure of correcting his results by means of the thermodynamically unpredictable cell where one of the cadmium electrodes dipped into a solution of magnesium sulfate containing no cadmium salt is only a minor objection. The chief point is that his results, according to the mass law, are equally in accord with the hypothesis of complete dissociation, or of partial dissociation, or of formation of any suggested proportion of complex ions, the last possibility being that which was shown in our previous communication to be true for these mixtures from the fact that the cadmium migrates toward the anode and is, therefore, not predominantly in the form of the positively charged cadmium ion.

Bronsted himself recognized this complete inconclusiveness or ambiguity and proceeded to make the experiments of his second paper[18] in which the chlorine electrode was dipped in two solutions of magnesium chloride of different concentration, the total concentration being made up to 4.0 N with magnesium sulfate in every case. Here Bronsted relied upon the fact that magnesium chloride is a ternary electrolyte and, therefore, would become completely dissociated at infinite dilution of magnesium chloride even in presence of the concentrated magnesium sulfate. To this standpoint no exception can be taken because more complicated modes of dissociation would merely obscure but not invalidate the final effect. However, Bronsted's numerical evaluation of his results is based upon the implicit assumption that a 0.0032 N magnesium chloride in 4.0 N solution of magnesium sulfate is 100% dissociated, and, if so, 0.1 N magnesium chloride is 99.3% dissociated. The assumption, however, begs the whole question, which is therefore seen to be one of opinion and not of experimental evidence. Migration data such as we adduce show, on the contrary, that magnesium, whether in chloride or sulfate, can be carried to the anode and, therefore, in such mixtures more of it bears a negative than a positive charge, a result fatal to any assumption of complete dissociation into simple ions.

Summary

1. In 0.05 M solutions of magnesium or rubidium sulfates, addition of a large proportion of the other sulfate causes the magnesium or rubidium to migrate away from the cathode toward the anode. In mixtures of ammonium iodide with excess of potassium iodide the movement of the ammonium may be practically suppressed. In mixtures of potassium chloride with excess of sodium chloride or of potassium nitrate with excess of sodium nitrate, the movement of the potassium may be considerably decreased.

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[18] J. N. Bronsted, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **3**, *No. 9, 14 (1920); Trans. Faraday Soc.*, **44,727** *(1928).*

2. The general conclusion is that strong electrolytes form undissociated molecules and complex anions; they differ only in degree from such an extreme case as that of cadmium iodide. Electrolytes would all seem to fall within a triangle whose corners represent extreme dissociation, extremely weak electrolytes and complete formation of complex ions, respectively.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. VIII. USE OF METHYL RED, ERIO GLAUCINE AND ERIO GREEN INDICATORS IN THE REACTION BETWEEN CERIC AND FERROUS IONS

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Introduction

A number of applications of ceric sulfate in volumetric analysis have been described recently.[1] The use of various organic substances, for example, methyl red, methylene blue and methyl orange, as irreversible oxidation-reduction indicators in the titration of trivalent antimony with ceric sulfate was proposed by Rathsberg.[2] We have shown that methyl red may be used as an indicator in the titration of hydroquinone with ceric sulfate.[3]

We have found that methyl red is an excellent indicator in the titration of ferrous salt with ceric sulfate or *vice versa.* Upon titration of a ferrous solution with ceric sulfate, the ferrous salt is oxidized first; a slight excess of ceric sulfate oxidizes the methyl red to a substance that is brownish in concentrated solution and yellow in very dilute solution. The oxidation product is destroyed upon standing in contact with an excess of ceric sulfate.

When ceric sulfate is being titrated with ferrous sulfate solution, the latter is added rapidly until the color of the ceric ion has almost disappeared. Methyl red is added, and is oxidized to the yellowish product. Upon further addition of ferrous salt, there is a transition from yellow to violet when a slight excess of ferrous salt is present. If phosphoric acid be added, the color change agrees well with the potentiometric end-point. The color change of methyl red is much more rapid than that of diphenylamine under the same conditions. In agreement with Willard and Young[4]

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[1] A bibliography is given in the preceding paper of this series, THIS JOURNAL, 52, 1443 (1930); reference to the older literature is given by Willard and Young, *ibid.*, 50, 1322 (1928). and by Furman, *ibid.*, 50, 755 (1928).

[2] Rathsberg, *Ber.*, 61, 1664 (1928).

[3] Furman and Wallace, THIS JOURNAL, 52, 1443 (1930).

[4] Willard and Young, THIS JOURNAL, 50, 1336 (1928).

we find that the use of diphenylamine is unreliable in the determination of cerium with ferrous sulfate.

During the progress of our work with methyl red there appeared two publications by Knop[5] in which he suggested the use of two triphenylmethane dyes, erio glaucine and erio green, as reversible oxidation–reduction indicators in the titration of ferrocyanide with permanganate. We have found that these indicators are excellent for certain titrations with, or of, ceric sulfate.

Experimental

Ceric sulfate solutions of approximately 0.1 or 0.05 N oxidizing power and 1 N in sulfuric acid were prepared from commercial hydrated ceric oxide (45% CeO_2) and were standardized potentiometrically against pure sodium oxalate.[6]

Methyl Red as Indicator.—Two-tenths g. of a Kahlbaum preparation was treated with 100 cc. of 6 N sulfuric acid. Nearly all of the material dissolved, and the slight residue was filtered off; 0.05 cc. of the solution is adequate for a titration.

Titration of Ferrous Iron with **Ceric** Sulfate.—The data are presented in Table I.

TABLE I

TITRATION OF APPROXIMATELY 0.1 *M* MOHR'S SALT SOLUTION WITH 0.1120 *M* CERIC SULFATE

Ferrous soln., *cc.*	25	25	25	25	50	50	10	10
Initial vol., cc.	50	100	235	50	150	200	50	100
H_2SO_4 concn., *N*	0.3	0.2	0.75	3.6	1.2	1.0	0.6	0.3
Ceric soln. used	22.36	22.38	22.34	22.35	44.64	44.62	8.92	8.93
Ceric soln. calcd.	22.32	22.32	22.32	22.32	44.64	44.64	8.93	8.93

The calculated values are based on the average of four concordant potentiometric determinations. In each case 0.05 cc. of indicator was used. If the solution is stirred vigorously by hand, there is a sharp end-point even when the indicator is added at the start of the titration. It is desirable, however, to add the indicator when the ceric sulfate has begun to be consumed slowly. The determinations of Table I do not show clearly what correction, if any, should be applied when 0.1 N solutions are used. From the results with 0.05 M solutions it seems safe to apply a correction of 0.03 cc. to be subtracted from the buret reading in the titration of 0.1 M solution, this correction being approximately half of that found in Table II.

In Determinations 1–4 the ceric solution was 0.0593 N, and in Nos. 5–8, 0.0552 N. The calculated values are based on sets of four concordant

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[5] Knop, Z. anal. Chem., **77**, 111 (1929); Knop and Kubeikova, *ibid.*, **77**, 125 (1929).

[6] The details of preparation, standardization and a description of the apparatus are given by Furman and Evans, THIS JOURNAL, 51, 1129 (1929).

TABLE II

TITRATION OF APPROXIMATELY 0.05 *M* FERROUS SOLUTION WITH 0.05 M CERIC SULFATE

	1	2	3	4	5	6	7	8
Initial volume, cc......	100	110	150	100	35	60	200	125
Initial acid concn., *N*.	0.5	0.7	0.3	0.6	0.2	0.2	0.3	1.2
Acid used...........	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	H_2SO_4	HCl	H_2SO_4
Ceric soln. used, cc ...	41.24	41.25	16.48	16.47	8.03	20.01	20.00	39.98
Ceric soln. calcd., cc..	41.20	41.20	16.42	16.42	8.00	19.96	19.96	39.92

potentiometric determinations. On the average 0.06 cc. of ceric sulfate needs to be subtracted from the buret reading in order to make the indicator values coincide with the potentiometric ones. When hydrochloric acid is present, the color change is not as sharp as in sulfuric acid solution, but the change is very distinct.

The methyl red end-point is satisfactory in solutions which have been reduced with stannous chloride in excess, the excess being destroyed with mercuric chloride. A solution of ferric alum in dilute sulfuric acid required per 25 cc.: 21.69, 21.70, 21.68 cc. of 0.0948 *N* ceric solution after stannous chloride reduction, and 21.70, 21.73, 21.71 cc. of the ceric solution after passage of 25-cc. portions through a Jones reductor.

If Mohr's salt is used as a secondary standard, the correction of 0.03 cc. of 0.1 N ceric solution brings the methyl red end-point in good agreement with the potentiometric.

Ceric sulfate vs. sodium oxalatc, N	0.1079	0.1081	0.1080
Mohr's salt used, g.	1.0502	1.3260	1.0072
Ceric solution uncorrected	24.85	31.33	23.82
Normality	0.1077	0.1079	0.1078
Applying 0.03 cc. corr., N =	0.1079	0.1080	0.1080

Titration of Ceric Sulfate with Ferrous Sulfate.—The ferrous sulfate is added until the solution is pale yellow (slight excess of ceric ion), 0.05 cc.

TABLE III

TITRATION OF 0.1073 N CERIC SULFATE WITH FERROUS SULFATE

Series I

Ceric sulfate used, cc,	25	25	25	10	10	10	Av per 25 cc.
Ferrous sulfate, cc.							
Methyl red	29.80	29.83	29.79	11.94	11.92	11.91	29.81
Potentiometric	29.87	29.85	29.85	11.96	11.93		29.86
Diphenylamine	29.85	29.89		11.90	11.91		29.81

Series II

Ceric solution used, cc.	25	25	25	25	
Ferrous sulfate, *cc.*					
Methyl red	30.02	30.04	30.03	30.02	30.03
Potentiometric	30.01	30.05	30.06		30.04
Diphenylamine	30.08	30.07	30.11	30.07	30.08

of methyl red is added, and immediately afterward 25 cc. of the sulfuric–phosphoric acid mixture (150 cc. of each concentrated acid per liter) which is used in Knop's[7] diphenylamine method. The yellow color of the solution becomes much less intense, but no precipitation of cerium phosphates occurs. The ferrous sulfate is added slowly until the solution suddenly becomes pale violet. Upon standing the violet color deepens. Some results are presented in Table III.

Five one-hundredths cc. of methyl red or 0.05 cc. of 1% diphenylamine was used. The behavior of diphenylamine is erratic, and the position of the end-point depends upon the speed of titration at the end-point.

Behavior of Methyl Red on Oxidation and Reduction.—This study is still in a preliminary stage as far as the mechanism of the reaction is concerned. A brief résumé of some qualitative experiments may be of interest. Ceric sulfate appears to be the only oxidizing agent which gives the intermediate oxidation product of methyl red under the conditions used in volumetric analysis. Bromate, permanganate and chlorine carry the oxidation so far that no colored product is formed on reduction with ferrous salt. The violet-colored substance is formed when the reduction is carefully performed with stannous chloride; sulfite, on the other hand, carried the reduction to a colorless stage.

Methyl red shows the same oxidation–reduction behavior after recrystallization from glacial acetic acid, as before purification.

The violet-colored reduction product is extracted from aqueous solution by ether to give an orange-red solution, and by benzene to give a violet-red solution. In the latter solvent methyl red forms an orange or yellow extract, although largely present in the red form in the strongly acid aqueous layer. Thus far it has not been possible to obtain the violet substance in a form pure enough for analysis.

Erio Glaucine and Erio Green Indicators—Erio Glaucine A (Schulz No. 506) and Alkali Past (erio) Green A were obtained from the National Aniline and Chemical Company, New York; 0.1% aqueous solutions were prepared, and 0.5 cc. of either solution was used for a single titration. Knop[7] states that the compositions of the rose-colored oxidation products are not known. Either indicator forms a greenish-yellow color in acid solution; in pure water the colors are blue and green, respectively. A very slight excess of ceric sulfate colors either indicator rose or red; in the presence of a ferric salt the color is orange or pale rose. There is a short time interval necessary for the development of the full color change at the end-point; the danger of over-titration is slight. The results are summarized in Table IV.

The determinations were made as closely together as possible, in point of time, with alternation of indicator and potentiometric determinations.

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[7] Knop, This Journal, 46, 263 (1924).

TABLE IV

USE OF ERIO GLAUCINE AND ERIO GREEN IN TITRATION OF FERROUS SULFATE WITH 0.0948 N CERIC SULFATE

Erio Glaucine Indicator

Ferrous sulfate, cc...	25	25	25	25	50	50	**Av.** per 25 cc.
Initial acid concn., *N*	0.7	3.0	0.35	3 N	2	2	
Acid	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	HCl	
Initial volume, cc	25	50	50	50	75	75	
Ceric sulfate, cc	23.05	23.04	22.99	23.00	45.99	43.98	23.01

Erio Green Indicator

Ferrous sulfate	25	25	25	25	50	50	
Initial acid concn., N.	0.7	3.0	3.0	0.75	2.0	2.0	
Acid........................	H_2SO_4	H_2SO_4	HCl	HCl	H_2SO_4	HCl	
Initial volume, cc	25	50	50	100	75	75	
Ceric solution, cc.	22.98	23.01	23.03	22.98	45.97	45.91	22.98

Potentiometric

Ferric solution, cc............	25	25	25	25	50	50	
Ceric solution used, cc.	22.99	23.03	23.00	23.03	45.98	45.89	22.99

There does not appear to be any correction to be applied in working with 0.1 *N* solutions.

The reverse titration was studied. It was found that either indicator could be added immediately before the start of a titration. The color was initially orange; when nearly all of the ceric ion had been reduced the rose tint predominated. At the end-point there was a sharp transition to yellow with a slight time interval needed for the color change.

TABLE V

TITRATION OF 0.1028 N CERIC SULFATE WITH FERROUS SULFATE

Erio Glaucine Indicator

Ceric solution, cc.........	10	10	10	25	25	Av. per 25 cc.
Initial H_2SO_4 concn., *N*...	1	0.67	0.7	1.4	1	
Initial volume, cc.........	40	65	100	60	85	
$FeSO_4$ used, cc...........	11.97	12.00	11.98	29.95	29.98	29.96

Erio Green Indicator

Ceric solution, cc.........	10	10	10	25	25	
Initial H_2SO_4 concn., N...	1	0.67	0.7	1.4	1	
Initial volume, cc.........	40	65	100	60	85	
$FeSO_4$ used, cc...........	11.99	11.96	11.98	29.95	29.95	29.95

Potentiometric

Ceric solution, cc.........	10	10	25	25	25	
$FeSO_4$ used, cc...........	11.99	11.98	29.99	29.99	29.95	29.98

Within the limits of error of these determinations there appears to be no indicator correction.

It seemed of interest to determine whether the presence of calomel and mercuric chloride would interfere with the functioning of the indicators. A solution of ferric alum, acidified with sulfuric acid, was prepared, and aliquot portions were reduced by the stannous chloride method with subsequent addition of excess of mercuric chloride. Portions of the solution were reduced by the Jones reductor, and an average of 23.09 cc. of 0.0945 N ceric sulfate was required per 25 cc. of alum solution.

TABLE VI

TITRATIONS AFTER REDUCTION WITH STANNOUS CHLORIDE

Erio Glaucine Indicator

Alum solution, cc.	25	25	25	10	10
Ceric solution found, cc.	23.05	23.13	23.09	9.23	9.22
Error, cc.	−0.04	+0.04	±0.00	±0.00	−0.01

Erio Green Indicator

Alum solution, cc.	35	25	10	10
Ceric solution found, cc.	23.11	23.08	9.22	9.24
Error, cc.	+0.02	−0.02	−0.01	+0.01

A number of other uses of erio glaucine and erio green in titrations with ceric sulfate are being studied.

Summary

Methyl red in dilute sulfuric acid solution may be used as indicator in the titration of ferrous ion with ceric, or ***vice versa.*** In the latter case the indicator must be added near the end-point, and phosphoric acid must bc present. A correction must be applied in the former titration.

A new behavior of methyl red upon mild oxidation–reduction treatment has been described.

Erio glaucine and erio green are excellent indicators for the titration of ferrous ion with ceric, or ***vice versa.*** No correction need be applied in either case with a 0.1 N standard solution.

The three indicators are satisfactory in hydrochloric acid solution as well as in sulfuric, and in the presence of calomel and excess of mercuric chloride.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

ACTIVITY COEFFICIENTS OF SODIUM, POTASSIUM AND LITHIUM CHLORIDES AND HYDROCHLORIC ACID AT INFINITE DILUTION IN WATER-METHYL ALCOHOL MIXTURES

BY GÖSTA ÅKERLÖF

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I. Introduction

The activity coefficients of a number of the alkali halides in pure aqueous solutions have recently been redetermined with great precision by Harned.[1] He used cells of the type

$$Ag/AgX/MeX\ (m_1)/Me_yHg/MeX\ (m_2)/AgX/Ag$$

where X designates the halide and Me the alkali metal present. In the present investigation cells of the same general type have been used, but the concentration of the electrolyte was the same on both sides of the cells and the composition of the solvent used as a variable

$$Ag/AgX/MeX\ (m_1)\text{ in water}/Me_yHg/MeX\ (m_1)\text{ in water–alcohol}/AgX/Ag$$

Through suitable recombining of these cells with those for pure aqueous solutions it was possible with the use of the Debye–Hückel activity function to calculate the activity coefficients of the electrolytes employed in the water–alcohol solutions. This also gave the means of determining the activity coefficients at infinite dilution in relation to the corresponding water value which was assumed to be unity in accordance with custom. As has been predicted by the simplest theory possible, it was found that within the errors due to uncertainties of the calculation and experimental difficulties, the logarithm of the activity coefficient at infinite dilution is approximately inversely proportional to the dielectric constant of the pure water–methyl alcohol mixtures. It is the first time this has actually been shown to be the case and therefore, although expected, it is of considerable importance.

II. Experimental Methods

The methyl alcohol used was free from acetone and aldehydes; the density corresponded very closely to the accepted value for pure, absolute alcohol. As the alcohol always was used in mixture with water a correction for the very small water content of the original product was considered unnecessary. All salts used were of the analyzed variety and further purification was not carried out. Hydrochloric acid was carefully redistilled as constant-boiling mixture and middle portions were used. All solutions

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[1] Harned, THIS JOURNAL, **51,** *416 (1929);* compare further MacInnes and Parker, *ibid.*, **37,** *1445 (1915)*; Allmand and Polack, J. *Chem.* Sac., **115,** *1020 (1919)*; Pearce and Hart, THIS JOURNAL, **43,** *2483 (1921);* Harned and Douglas, *ibid.*, **48,** *3095 (1926).* Measurements with hydrochloric acid: Ellis, *ibid.*, **38,** 737 *(1916);* Noyes and Ellis, *ibid.*, 39, *2532 (1917);* Linhart, *ibid.*, **39,** *2601 (1917);* Scatchard, *ibid.*, **47,** *641 (1925).*

were generally made up through diluting standard solutions with calculated amounts of water and alcohol. All concentrations of the electrolytes are given in molality per 1000 g. of the solvent. The methyl alcohol concentration is expressed in weight per cent.

Silver–silver chloride electrodes[2] were prepared from silver deposited on a small platinum-spiral through decomposition of silver oxide paste at 500°. The electrolysis in one molal hydrochloric acid was carried out with 10 milliamperes during two hours. Hydrogen electrodes[2] were obtained through electrolysis with a small platinum-foil in an approximately 1%, strongly acid, $PtCl_4$ solution. The amount of current used was about 0.1 amp. per sq. cm. of surface of the foil during six minutes. The alkali metal amalgams were made by the method described by Harned.[2b] The lithium amalgam was found to work fairly well without any special precautions. The design of the amalgam cells employed is given in Fig. 1. The procedure for measurements of these cells has been described sufficiently elsewhere.[2,3] The temperature for all measurements was 25.00°.

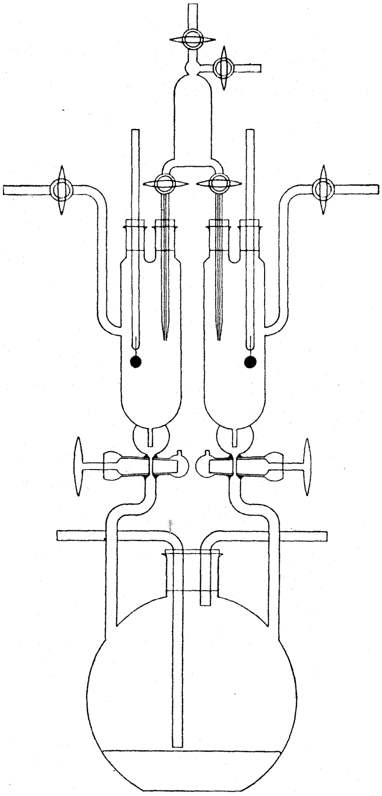
Fig. 1.—Apparatus for the amalgam cells.

III. Accuracy of the Results

The electromotive force of the amalgam cells was wholly due to the differences in the composition of the solvent used in the two half cells. The amount of solvent employed in making up the solutions varied between 600 to 800 g. Before the cells were filled the two solutions that were to be used were boiled in vacuum at room temperature during two to four minutes. The salt concentration of the pure water solution changed very slightly but the evaporation from the alcohol solution was naturally considerably greater. If the amount of solvent evaporated had been the same on both sides of

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[2] A review of the method* and the literature for Ag/AgCl electrodes is given (a) by Harned, Ref. 1; regarding hydrogen electrodes compare also Harned and Åkerlöf, *Physik. Z.*, 27, 411 (1926); (b) Harned, THIS JOURNAL, 47, 676 (1925); preparation of lithium amalgam, Harned and Swindells, ibid., 48, 126 (1926).

[3] Åkerlöf, *ibid.*, 48, 1160 (1926).

the cell the effect of the electromotive force could scarcely have been noticed even with a very high measuring accuracy. To compensate for the larger loss on the alcohol side a slight excess of pure alcohol was added. The excess increased somewhat with the alcohol concentration and corresponded sufficiently closely with the actual loss. For dilute or fairly concentrated wateralcohol mixtures (up to 60%) this precaution worked very well. At still higher alcohol concentrations the difficulties in obtaining good results increased very rapidly. Usually the same measurement had to be repeated with new solutions three or four times and then their mean used. The measurements were carried out with a series of water-alcohol mixtures differing by 10% in alcohol content. Dividing the electromotive force by the alcohol content and plotting the values obtained against it usually gave a very smooth curve at lower alcohol concentrations. At higher ones the deviations were sometimes quite large, indicating possible errors of 2–3 millivolts. Up to 50% alcohol the errors seemed hardly to exceed 0.2–0.3 of a millivolt but systematic errors might easily have been present. For the measurements with solutions of hydrochloric acid errors due to evaporation of alcohol were unlikely to occur. Immediately before the hydrogen entered the cell it had passed through a long bubbling tower almost completely immersed in the water of the thermostat and containing about 200 cc. of the solution used. The measurements with these solutions may therefore have only the ordinary, apparent errors of 0.1--0.2 of a millivolt through the entire series.

IV. The Calculation of the Results

The limiting function of Debye–Hückel for the logarithm of the activity coefficient of a strong electrolyte is given by the well-known equation

$$\ln \gamma = -\frac{\epsilon^2 \cdot z_i^2}{k \cdot T \cdot D \cdot 2} \sqrt{\frac{8\pi \cdot N \cdot \epsilon^2 \cdot z_i^2 \cdot m}{K \cdot T \cdot D}} \text{ or } \ln \gamma = -u\sqrt{2m} \qquad (1)$$

where ϵ is the electron charge, k the Boltzmann constant, T the absolute temperature, D the dielectric constant of the medium, N the number of Avogadro, k the "mean distance of ionic approach," z_i the valence number of ions of the ith kind and m the concentration of the electrolyte. Recently Gronwall, LaMer and Sandved[4] have extended this simplified equation to the so-called terms of higher order. They showed that in cases with symmetrical ions, where very small or negative distances of ionic approach were obtained with the original Debye–Hückel theory, their extended form gave positive and constant values, which seemed to be reasonable. However, their improved equations could only be used for very dilute solutions where the dielectric constant of the medium might be assumed to remain practically unchanged with varying concentration of the electrolyte. In this concentration range the electromotive force methods of determining

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[4] Gronwall, LaMer and Sandved, *Physik. Z.*, 29, **338** (1928).

activities are more or less unreliable and as we therefore were forced to use far higher concentrations, the equations mentioned could not be used in their present form. To obtain an equation which may be used for a large concentration range, Hückel[5] deduced an equation for the influence of the electric charges of the ions of the electrolytes. The fundamental assumption made was that the total change of the dielectric constant of the medium decreased linearly with increasing concentration. In a number of cases where the ions present had small dipole moments, this assumption was found to lead to negative dielectric constants in only fairly concentrated solutions, which is an impossibility. Nevertheless, a simplified form of Hückel's equation was shown by Hückel, Scatchard, Harned, Åkerlöf and others to be able to express the results of the activity measurements with great precision over a very large concentration range. The general form of the equation employed is

$$\log \gamma = -u\left(\frac{\Sigma\nu_i z_i^2}{\Sigma\nu_i}\right)^{3/2} \cdot \frac{\sqrt{\Sigma\nu_i c_i}}{1 + A\sqrt{\Sigma c_i z_i^2}} + B\Sigma c_i z_i^2 - \log\left(1 + \frac{M}{1000}\Sigma m_i\right)\ldots \quad (2)$$

where u is a universal constant, A and B are empirical constants, M is the molecular weight of the solvent, m and c are the concentration of the electrolyte in molality and molarity, ν_i and z_i the number and valence of ions of the ith kind. So far in all cases where this equation has been used the theoretical value of the constant u has been employed, both for aqueous and non-aqueous solutions. As an example may be mentioned the calculation of Lucasse[6a] of the activity coefficient of hydrochloric acid in methyl alcohol from the measurements of Nonhebel and Hartley,[6b] in ethyl alcohol from those of Harned and Fleysher.[6c] Lucasse concluded that a very good agreement had been obtained between observed and calculated values. The quite appreciable deviations, especially at very low acid concentrations, were attributed to experimental difficulties such as hydrogen electrode errors, etc.

When Equation 2 was applied to some of the measurements presented here, it was soon found that it could not be used with the theoretical u-values. Since most of the results were obtained for fairly dilute solutions, the term $B2m$ from Equation 2 was neglected in the case of potassium and sodium chloride solutions on account of its assumed smallness. As variables u and A were used. The measurements with lithium chloride solutions were extended over quite a large concentration range. In this case the influence of the term $B2m$ is quite considerable at higher concentrations and could not be neglected. Therefore the u-values were first determined from measurements at lower concentrations and then the A and B values from a series of results at higher ones. As the difference between calculated

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[5] Hückel, *Physik. Z.*, 26, 93 (1925).

[6] (a) Lucasse, *Z. physik. Chem.*, **121, 254** (1926); (b) Nonhebel and Hartley, *Phil. Mag.*, [6] 50, 298, 729 (1925); (c) Harned and Fleysher, THIS JOURNAL, 47, 82 (1925).

and theoretical u-values increases rapidly with increasing alcohol concentration, the u-values for lithium chloride solutions were calculated only for the two highest alcohol concentrations employed and then interpolated to give a curve of the same form as the curve for the theoretical values. For hydrochloric acid this method of calculation was found to be unnecessary and in this case the theoretical u-values were used.

The determination of the variables u, A and B each required a separate electromotive force value that was to be obtained from the measurements in the following manner. Consider the three cells

I Ag/AgCl/MeCl (m_1)/Me$_y$Hg/MeCl (m_2)/AgCl/Ag
II Ag/AgCl/MeCl $(m_1, a\%$ alc.)/Me$_y$Hg/MeCl (m_1)/AgCl/Ag
III Ag/AgCl/MeCl $(m_2, a\%$ alc.)/Me$_y$Hg/MeCl (m_2)/AgCl/Ag

The electromotive forces of these three cells may be expressed by the equations

$$E_1 = \frac{RT}{NF} \ln \frac{\gamma_1 . m_1 \text{ (water)}}{\gamma_2 m_2 \text{ (water)}} \tag{3a}$$

$$E_2 = \frac{RT}{NF} \ln \frac{\gamma_1^* . m_1^* \text{ (alc.)}}{\gamma_1 \cdot m_1 \text{ (water)}} \tag{3b}$$

$$E_3 = \frac{RT}{NF} \ln \frac{\gamma_2^* \cdot m_2^* \text{ (alc.)}}{\gamma_2 . m_2 \text{ (water)}} \tag{3c}$$

An asterisk marks activity coefficients and concentrations in alcohol-water solutions. Subtraction of the second equation from the first one and addition of the third gives

$$E_4 = \frac{RT}{NF} \ln \frac{\gamma_2^* . m_2^* \text{ (alc.)}}{\gamma_1^* . m_1^* \text{ (alc.)}} \tag{3d}$$

Finally there is also a measurement necessary for the elimination of E_0 according to the equation

$$E_4 - E_0 = \frac{RT}{NF} \ln \gamma \cdot m \tag{3e}$$

For potassium, sodium and lithium chlorides the values of E_1 were calculated from the measurements of Harned. The measurements for hydrochloric acid gave directly the values of E_4. As previously indicated it has been customary to express the concentrations for these calculations in two units, molar and molal. In order to avoid a rather unnecessary labor, all concentrations in the following will always be expressed and used as molality. This makes the logarithmic end term in Equation 2 unnecessary for the calculations. The measurements were generally used interpolated from curves.

V. Experimental Results

In Tables I, II, III and IV are given the results of the measurements and calculations with potassium, sodium and lithium chlorides and hydrochloric acid, respectively. All measurements with cells containing hydrogen electrodes are corrected to a partial hydrogen pressure of 760 mm. of mercury. The vapor pressures of the water--methyl alcohol mixtures without electrolytes present were obtained from the measurements of Konowalow[7] in the following manner. The values for constant alcohol concen-

TABLE I

ELECTROMOTIVE FORCE MEASUREMENTS AND ACTIVITY COEFFICIENTS FOR POTASSIUM CHLORIDE IN WATER–METHYL ALCOHOL SOLUTIONS

1. E. m. f. measurements and empirical constants derived from them. The e. m. f. values refer to the cells: Ag/AgCl/KCl (m) in pure water/K_yHg/KCl (m) in water–alcohol/AgCl/Ag.

Alc., wt %	E 0.02 m	E 0.05 m	E 0.10 m	E 0.50 m	u	A	B
0	0 00000	0 00000	0 00000	0 00000	0 357	0 737	0 0112
10	01807	01747	.01705	01612	,499	1.20	. ..
20	.03640	03510	.03436	03240	645	1 50	....
30	05508	05310	.05202	,04894	.880	2 00	....
40	.07470	07152	.07012	.06600	1 270	2 75	....
50	.09420	.09075	.08925	,08350	1.72	3 75	....
60	.1158	.1116	.1097	.1028	2.87	5.00	. ..
70	.1402	.1348	.1326	....	4.37	6 50	....
80	.1681	.1603	.1577	....	6.72	8.25	....
90	.1968	.1883	.1854	....	10 93	10.50	....

2. Activity coefficients at infinite dilution and at concentrations used

Alc., wt. %	γ0 02 m calcd.	70.02 m obs.	γ0 05 m calcd.	γ0 05 m obs.	γ0.10 m standard	γ0 50 m calcd.	γ0.50 m obs.
0	0 867	0 867	0 812	0 812	0 762	0 639	0.639
10	.831	.831	.767	.769	716	(.593)	.611
20	.796	.796	.727	.726	.672	(.552)	.585
30	.749	.749	.675	.674	.620	(.509)	.552
40	.686	.691	.610	.609	.556	(.458)	.506
50	.636	.646	.564	.566	516	(434)	.484
60	.517	.515	.445	.443	.402	(.333)	.385
70	.416	.417	.352	351	.316	..	..
80	,312	.312	.258	.257	.229	..	..
90	.197	.197	.159	.156	.139	..	..

3. E. m. f. measurements by Harned for pure aqueous solutions

KCl m	E obs.	E calcd.	γobs.	γcalcd.
0.02	....	−0 07605	0 867	0.867
.05	....	− .03237	.812	.812
.10	0 00000	.00000[a]	762	.762
.20	.03198	.03187	710	.709
.50	.07390	.07365	.642	.639
1.00	.10565	.10565[a]	.596	.596
1.50	.12459	,12493	.574	.578
2.00	.13877	,13903	.568	.571
2 50	.15018	.15045	.567	.570
3.00	.15976	.15976[a]	570	.570

[a] These measurements used for the calculation of the empirical constants.

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[7] Konowalow, *Wied. Ann.*, **14,** 34 (1881); Landolt-Börnstein, "Tabellen," 5th ed., 1923, Vol. II, p. 1398; Foote and Dixon, *Am. J. Sci.*, [5] **17,** 146 (1929).

TABLE II

ELECTROMOTIVE FORCE MEASUREMENTS AND ACTIVITY COEFFICIENTS FOR SODIUM CHLORIDE IN WATER–METHYL ALCOHOL SOLUTIONS

1. E. m. f. measurements and empirical constants derived from them. The e. m. f. values refer to the cell: Ag/AgCl/NaCl (m) in pure water/Na$_y$Hg/NaCl (m) in water–alcohol/AgCl/Ag.

Alc., wt. %	E 0.02 m	E 0.05 m	E 0.20 m	E 0.50 m	u	A	B
0	0.00000	0.00000	0.00000	0.00000	0.357	0.832	0.0232
10	.01777	.01732	.01681	.01641	.420	1.05	
20	.03568	.03475	.03370	.03290	.503	1.12	....
30	.05402	.05241	.05079	.04965	.603	1.30	....
40	.07268	.07045	.06816	.06670	.733	1.50	....
50	.09215	.08935	.08610	.08425	.904	1.75	
60	.1129	.10974	.10518	.10272	1.15	2.00	....
70	.1357	.1309	.1257	.1228	1.46	2.50	....
80	.1621	.1570	.1487	.1459	1.97	3.00	....
90	.1910	.1836	.1744	....	2.80	3.90	

2. Activity coefficients at infinite dilution and at concentrations used

Alc. wt. %	γ0.02 m calcd.	γ0.02 m obs.	γ0.05 m standard	γ0 20 m calcd.	γ0.20 m obs.	γ0.50 m calcd.	γ0.50 m obs.
0	0.871	0 871	0 818	0 727	0.727	0.673	0.673
10	.852	.852	.795	693	.699	.624	.643
20	.828	.827	.763	651	.664	.579	606
30	.802	.804	.732	.618	.630	.547	.571
40	.771	.773	.696	.578	.591	.509	.532
50	.735	.735	.655	.535	.545	.469	.488
60	.685	.678	.599	.477	.486	.414	.430
70	.639	.645	.552	.439	.443	383	.388
80	.567	.563	.479	.372	.362	.322	.318
90	.485	.493	.401	.317	.298	..	..

3. E. m. f. measurements by Harned for pure aqueous solutions

NaCl m	E obs.	E calcd.	γobs.	γcalcd.
0.02	....	−0.07660	0.871	0.871
.05	....	− ,03270	.818	.818
.10	0.00000	.00000[a]	.773	.773
.20	.03247	.03242	.727	.727
.50	.07566	.07560	.673	.673
1.00	.10957	.10957[a]	.652	.652
1.50	.13033	.13063	.651	.655
2.00	.14621	.14640	.666	.668
2.50	,15923	.15930	.686	.687
3.00	.17037	.17041[a]	.711	.711

[a] These measurements used for the calculation of the empirical constants.

tration at varying temperature were interpolated for 25°. Then the curve obtained was used for interpolation to the alcohol concentration desired. The vapor pressure for pure methyl alcohol at 25° was taken from the measurements of Foote and Dixon.[7] The decrease in vapor pressure on addition of the electrolytes used was calculated from Raoult's law assum

TABLE III

ELECTROMOTIVE FORCE MEASUREMENTS AND ACTIVITY COEFFICIENTS FOR LITHIUM CHLORIDE IN WATER–METHYL ALCOHOL SOLUTIONS

1. E. m. f. measurements and empirical constants derived from them. The e. m. f. values refer to the cell: Ag/AgCl/LiCl (*m*) in pure water/Li_xHg/LiCl (*m*) in water–alcohol/AgCl/Ag.

Alc., wt., %	E 0.02 m	E 0.05 m	E 0.10 m	E 0.50 m	E 1.00 m	*u*	*A*	*B*
0	0.00000	0.00000	0.00000	0.00000	0.00000	0.357	0.808	0.0611
10	.01280	,01188	.01158	,01085	.01091	.411	.700	.077
20	,02578	,02386	,02322	,02148	.02190	.476	.700	.086
30	,03876	,03603	,03507	.03240	.03300	.551	.730	,100
40	,05208	,04848	,04708	,04326	.04424	.640	.800	.100
50	,06575	,06180	.05965	.05530	.05595	.748	.890	.104
60	.08082	.07584	,07301	,06640	.06828	.887	.950	,115
70	.09730	.09107	,08715	,08005	.08134	1.07	1.05	.111
80	.1150	.1095	.1029	,09404	.09552	1.33	1.20	.090
90	.1371	.1276	.1204	.1087	.1109	1.80	1.60	.080

2. Activity coefficients at infinite dilution and at concentrations used

Alc., wt., %	γ0.02 m calcd.	γ0.02 m obs.	γ0.05 m calcd.	γ0.05 m obs.	rO.10 m stand.	γ0.50 *m* calcd.	γ0.50 *m* obs.	γ1.00 *m* calcd.	γ1.00 *m* obs.
0	0.873	0.873	0.824	0.824	0.785	0.731	0.731	0.770	0.762
10	.853	.854	.798	.792	.750	.684	.689	.728	.727
20	.832	.836	.768	.760	.716	.640	.645	.682	.684
30	.809	.815	.738	.730	.683	.605	.603	.656	.643
40	.783	.790	.705	.695	.645	.555	.557	.596	.599
50	.753	.757	.670	.661	.605	.511	.516	.550	.552
60	.717	.709	.625	.616	.555	.457	.454	.495	.496
70	.672	.674	.572	.563	.497	.388	.403	.410	.435
80	.615	.602	.506	.510	.427	.306	.334	.304	.363
90	.538	.542	.427	.426	.352	.244	.261	.240	.287

3. E. m. f. measurements by Harned for pure aqueous solutions

LiCl m	E obs.	E calcd.	robs.	γcalcd.
0.02	...	–0.07725	0.873	0.873
.05	...	– ,03313	.824	.824
.10	0.00000	.00000"	.785	.785
.50	.07900	.07900[a]	.731	.731
1.00	.1168	,11733	.762	.770
2.00	.1624	.16292	.926	.936
3.00	.1958	.19580[a]	1.183	1.183

[a] These measurements used for the calculation of the empirical constants.

complete dissociation. The correction of this decrease with the activity function is entirely negligible. The interpolated vapor pressures of water–methyl alcohol mixtures at 25° and their values at various concentrations of the electrolyte added are given in Table V.

A graphical representation of the results obtained for lithium chloride solutions is shown in Fig. 2. This figure gives also a good conception of the corresponding curves for potassium and sodium chloride and hydrochloric acid, because the distribution of these curves with varying alcohol

TABLE IV

ELECTROMOTIVE FORCE MEASUREMENTS AND ACTIVITY COEFFICIENTS FOR HYDROCHLORIC ACID IN WATER–METHYL ALCOHOL SOLUTIONS

1. E. m. f. measurements and empirical constants derived from them. The measurements were carried out for the cell: H_2/HCl (m), alc.–wat./AgCl/Ag.

Alc., wt., %	*E* 0.02 *m*	*E* 0.05 *m*	*E* 0.50 *m*	*u*[b]	A	*B*
0	0 4292[a]	0 3849[a]	0.2712[a]	0 357	0 984	0.0604
10		. .		.382		. .
20	.4191	.3753	.2621	.420	.99	076
30	4135	3700	.2578	.465	.99	085
40	.4075	3644	.2534	.517	1 00	.094
50	.4005	3579	.2483	.582	1 00	103
60	3915	3496	2417	.662	1.00	.112
70	3806	3395	2337	.760	0.98	.120
80	3637	3237	2206	.887	0 95	.128
90	.3292	2902	.1910	1.050	1 10	.097

[a] These e. m. f. values calculated from the measurements of Scatchard. [b] The theoretical u-values used. All e. m. f. values corrected to 760 mm. partial hydrogen pressure.

2. Activity coefficients at infinite dilution and at concentrations used

Alc., wt., %	γ0 02 *m* calcd	70.02 m obs.	γ0 05 m standard	γ0 50 *m* calcd.	γ0 50 m obs.
0	0 877	0 877	0 831	0 759	0 759
10					. .
20	857	860	806	733	730
30	843	.846	786	710	698
40	828	831	.768	685	.666
50	808	811	.742	649	627
60	784	.788	.711	604	581
70	755	758	674	545	529
80	718	.719	627	471	466
30	679	679	.580	395	.400

3 E m f measurements by Scatchard for pure aqueous solutions

HCl m	*E* obs	γcalcd	γobs.
0 01002	0 46376[a]	0 905	0 905
05005	38568	831	.828
09834	35316	797	.794
2030	31774[a]	767	767
3063	29332	757	754
3981	28407	756	753
5009	27197	759	757
6367	25902	769	767
1 0008	23290	812	.810
1 5346	20534[a]	.903	.903

[a] These measurements used for the calculation of the empirical constants.

concentration is very similar for the four electrolytes mentioned. Figure **3** gives an idea of the variation in distribution of the activity coefficient curves for potassium and sodium chlorides and hydrochloric acid at various alco-

TABLE V

TOTAL NUMBER N OF MOLES OF WATER AND METHYL ALCOHOL IN 1000 G. OF THE WATER–ALCOHOL MIXTURES, VAPOR PRESSURES IN MM. OF MERCURY AT 25° OF THE PURE MIXTURES AND WITH SUCCESSIVELY 1, 2, 3 AND 4 MOLES OF A UNI-UNIVALENT ELECTROLYTE ADDED. PRESSURE, p, MM.

		Concentration of electrolyte added				
Alc., wt. %	N	0 m, p	1 m, p	2 m, p	3 m, p	4 m, p
0	55.55	23.7	22.9	22.1	21 2	20.3
10	53.06	32.7	31.5	30.2	29.0	27.8
20	50.64	41.6	39.9	38.3	36.7	35.0
30	48.21	50.6	48.5	46.4	44.3	42.2
40	45.78	59.5	56.9	54 3	51.7	49.1
50	43.42	68.6	65.4	62 3	59.1	56.0
60	40.92	76.8	73.0	69.3	65.5	61.8
70	38.49	86.5	82.0	77.5	73.0	68.5
80	35.95	97.6	92.2	86.7	81.3	75.9
90	33.62	111.5	104.9	98.2	91.6	85.0
100	31.19	126.1	118.0	109.9	101.8	93.7

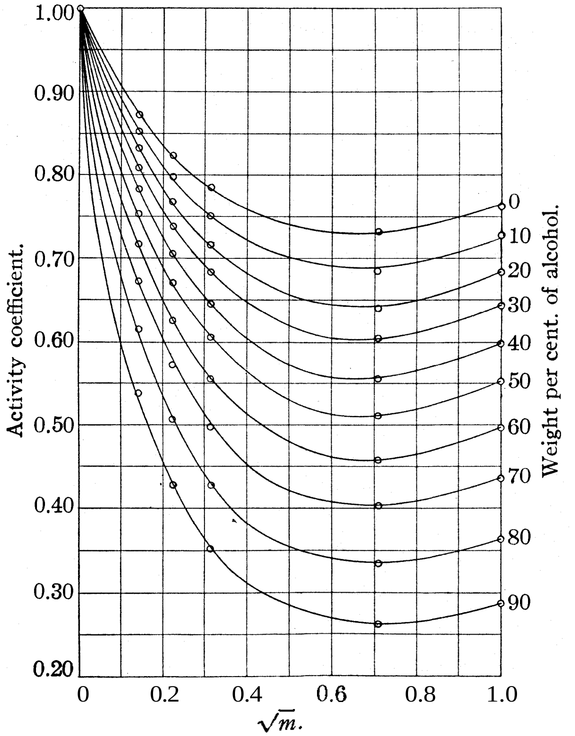

Fig. 2.—Curves for the activity coefficient of lithium chloride in water–methyl alcohol mixtures. The top curve is the one for pure water; then follow in order those for 10, 20. . . .etc., weight per sent. of alcohol.

hol concentrations in relation to each other. The figure shows that the order of distribution of the curves for the different electrolytes remains unchanged although their dispersion with increasing alcohol concentration changes by a very large amount. In this connection might be mentioned the result of a number of measurements of the activity coefficient of hydrochloric acid in acid–sodium chloride solutions at varying constant total molality and at varying alcohol concentration. The curves for the logarithm of the activity coefficient as plotted against the acid concentration

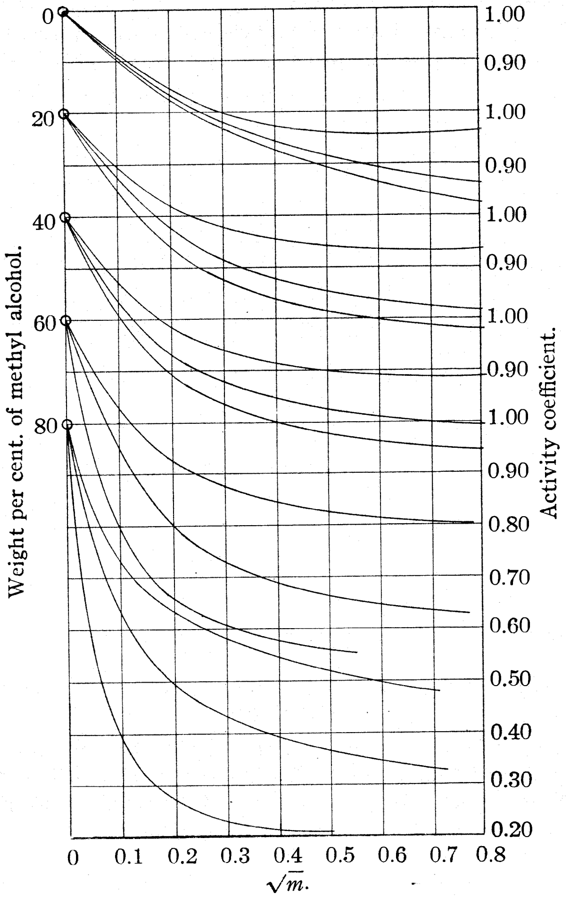

Fig. 3.—Distribution of the activity coefficient curves for potassium, sodium and hydrogen chloride in water–methyl alcohol mixtures. For each set of three curves the top one is always for hydrochloric acid, the middle one for sodium chloride. The scale is successively moved down in such a way that for a given water–alcohol mixture the circle corresponds to unity.

are straight lines and their slope is a constant independent of the total molality and alcohol concentration. In other words, strong electrolytes in alcohol solutions seem to show also in this respect the same general behavior, that has been demonstrated to be valid for water by Harned and Åkerlöf,[2a] Harned and Harris[8] and others.

Figure 4 gives the curves for the logarithm of the activity coefficients at infinite dilution in relation to unity for pure water as plotted against the inverse values of the dielectric constants of the pure water–methyl alcohol mixtures. The values for the dielectric constants were obtained from the measurements of Drude.[9] Since he found a linear variation of these constants with the alcohol concentration in weight per cent, and the temperature coefficient is not particularly well known, the pure water value was interpolated to 25°, the one for the pure alcohol taken as given by Drude for 19° and then interpolation was carried out linearly. A summary of all values used for Fig. 4 is given in Table VI. The values for log γ_∞ given in this table were calculated from the measurements for 0.02 molal solutions

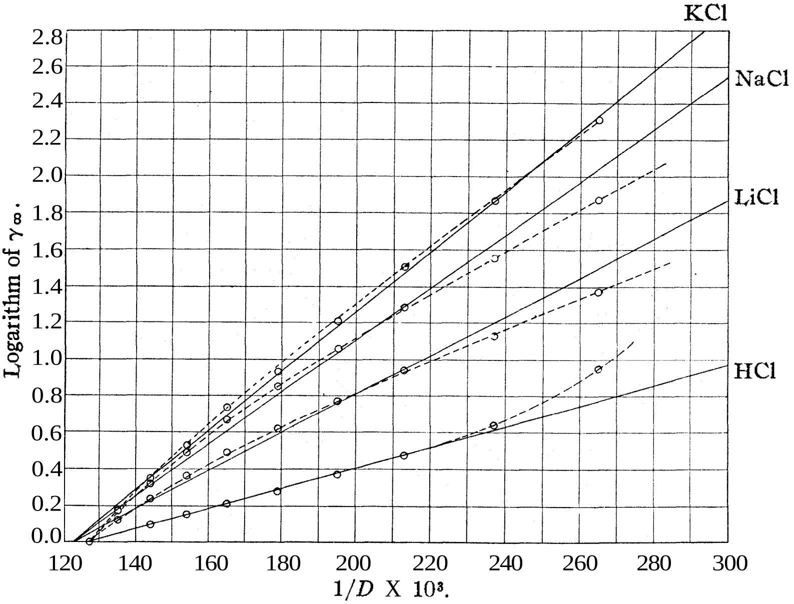

Fig. 4.—Curves for the logarithm of the activity coefficients of potassium, sodium, lithium and hydrogen chlorides at infinite dilution in water–methyl alcohol mixtures as plotted against the inverse values of the dielectric constants of these same mixtures. The dotted lines correspond to even curves through as many experimental points as possible.

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[8] Harned and Harris, This Journal, 50, 2633 (1928).

[9] Drude, *Z. physik. Chem.*, 23, 267 (1897); compare also "International Critical Tables," 1929, Vol. VI, p. 100.

in the following manner. The electromotive force values for the concentration mentioned gave first the ratios between the activity coefficients in pure water and the water–methyl alcohol mixtures, the last two values both related to unity at infinite dilution. Multiplication of the ratio obtained with the activity coefficient for 0.02 molal solutions in pure water and division with the corresponding value in water–alcohol gave for the alcohol mixture the desired value at infinite dilution.

Table VI

Mole Fraction of Methyl Alcohol *n*, Dielectric Constants *D*, their Inverse Values 1/*D* for the Pure Water–Alcohol Mixtures, Activity Coefficients of Potassium, Sodium and Lithium Chlorides and Hydrochloric Acid at Infinite Dilution in the Same Water–Alcohol Mixtures in Relation to the Corresponding Water Value Assumed to Be Unity

Alc., wt., %	n	D	$1/D$	KCl log γ_∞	NaCl log γ_∞	LiCl log γ_∞	HCl log γ_∞
0	0 0000	78.8	0 0127	0 000	0 000	0 000	0 000
10	0588	74 2	0135	.171	.160	.118	..
20	,1232	69 7	0144	345	.324	239	.095
30	.1941	65 1	.0154	.528	.492	.361	.150
40	.2725	60 6	.0165	.733	.667	.487	.208
50	.3608	56.0	.0179	.931	.853	.620	.278
60	.4574	51 4	.0195	1 204	1.059	.769	.367
70	.5673	46 9	.0213	1 504	1 282	.936	476
80	.6941	42.3	.0237	1 866	1.557	1.124	.640
90	.8350	37 8	.0265	2 307	1 870	1 369	.956
100	1 0000	33 2	.0301	...	...	..	..

Discussion

The purpose of the present investigation was primarily to obtain the curves for the activity coefficient of the electrolytes used at infinite dilution as a function of the composition and dielectric properties of the solvent. To gain this result it was considered as fully justified to employ the simplest methods possible, although those selected appear to have a large theoretical disadvantage. The Debye–Hückel theory gives as a limiting function for the logarithm of the activity coefficient of a strong electrolyte in very dilute solutions: $\log \gamma = -u\sqrt{2m}$. In the case of aqueous solutions it has generally been possible to use the theoretical value for the constant u. The instances in which a very small or even negative distance of ionic approach was obtained may be due to neglect of the higher terms. Actually Gronwall, LaMer and Sandved showed for the measurements of Bray[10] with zinc sulfate solutions that a positive, constant and reasonable limiting distance could be calculated from their extended theory.

In the case of the measurements presented in this paper for potassium and sodium chloride solutions, it proved to be impossible to use the theoretical u-values of the limiting function. The equation of Gronwall, La-

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[10] Bray, This Journal, 49, 2372 (1927).

Mer and Sandved, which should be applied only to electrolytes having anions and cations of equal valence has the following form:

$$\ln \gamma = -\frac{\epsilon^2 \cdot z^2 \cdot X}{2 \cdot k \cdot T \cdot Da(1 + X)} + \sum_{m=1}^{\infty} \left(\frac{\epsilon^2 \cdot z^2}{k \cdot T \cdot D \cdot a}\right)^{2m+1} \cdot \left[\frac{1}{2} X_{2m-1}(x) - 2m Y_{2m-1}(x)\right]$$

where a is the ionic diameter, assumed to be the same for both positive and negative ions, X and Y are very complicated functions of x = Ha,' where

$$H = \sqrt{\frac{8\pi \cdot N \cdot \epsilon^2 \cdot z^2 \cdot C}{1000 \cdot k \cdot T \cdot D}}$$

This equation might have given positive and constant ionic distances, but aside from the large difficulties for practical use, widely varying values would have been obtained for the different electrolytes used and, further, as log γ as a first approximation is inversely proportional to the dielectric constant of the medium, the concentration range over which this formula may be regarded as valid decreases rapidly with increasing alcohol concentration. Therefore, it seemed to be far simpler to use u as a variable even though this procedure brings in an apparent theoretical disadvantage. On account of the very large differences between theoretical and calculated u-values for potassium chloride solutions, the results for sodium and lithium chloride were treated in a manner similar to that for the first mentioned electrolyte. A graphical picture of the change of the u-values for the different electrolytes is shown in Fig. 5. The curve for the potassium chloride solutions deviates with increasing alcohol concentration very much from the theoretical one. Those for sodium and lithium chloride come considerably nearer the one for hydrochloric acid, which is the same as the curve given by the theory. The activity coefficients calculated in the manner described above from the empirical constants obtained agree in most cases very well with the observed values. The A- and B-values do not always give smooth curves but this should not be taken too seriously

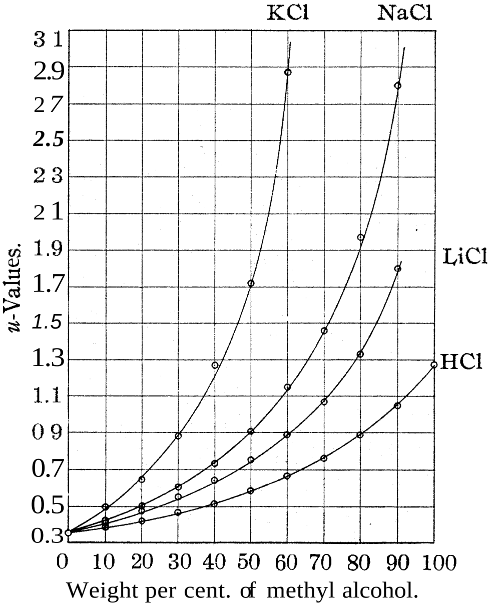

Fig 5.—Curves for the u-values used for potassium, sodium, lithium and hydrogen chlorides in water–methyl alcohol solutions. The theoretical curve is identical with the one for hydrochloric acid

on account of the disturbing influence of small experimental errors in the electromotive force measurements.

According to Debye and Hückel, in very dilute solutions the potential of one ion with respect to another of opposite sign is approximately inversely proportional to the dielectric constant of the medium and the distance between the ions. If we in our case assume that in very dilute solutions the distance two ions may approach reaches a limiting value independent of the properties of the solvent, then the logarithm of the activity coefficient of the electrolytes employed would at infinite dilution give a constant ratio with the dielectric constant of the medium. The dotted lines in Fig. 4 give the experimental curves for log γ_∞ when plotted against $1/D$. Considering the uncertainty of both the electromotive force and dielectric constant measurements as they were obtained from a single series of experiments, the deviations of the dotted lines from linearity may be regarded as fairly small at alcohol concentrations up to 80%. Above this concentration, especially, hydrochloric acid begins to show large deviations and for pure alcohol the measurements of Nonhebel and Hartley give a point that is very far above the one indicated by the extended straight line for lower alcohol concentrations. In Fig. 6 log γ_∞ is plotted against the mole fraction of the alcohol. In this case it seems to be possible that the deviations from straight lines may be attributed to experimental errors except for hydrochloric acid at high alcohol concentrations. From the

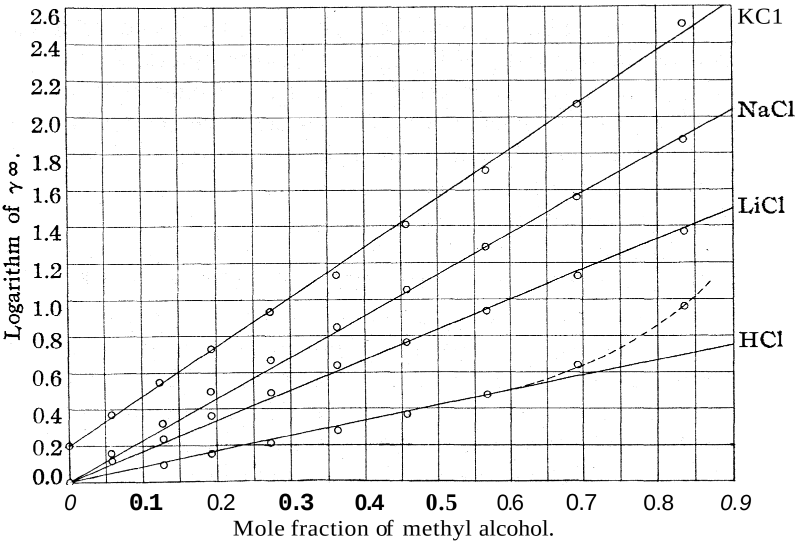

Fig. 6.—Curves for the logarithm of the activity coefficients of potassium, sodium, lithium and hydrogen chlorides at infinite dilution in water–methyl alcohol mixtures as plotted against the mole fraction of alcohol.

known activities of potassium and sodium chloride as extrapolated from the measurements of Harned for the saturated solutions of these salts in pure water, their solubilities in pure methyl alcohol give the corresponding activity coefficients in this solvent, because the activity of the solid salt is constant. The values thus obtained give, when extrapolated to zero salt concentration, coefficients which agree quite well with those predicted through extension of the straight lines in Fig. 6 to pure alcohol solutions. The solubility of lithium chloride in pure water is far too high to give a reasonably safe value for the activity at the saturation point and consequently also for the activity coefficient at infinite dilution in pure methyl alcohol, but at least the order of distribution of this point in relation to the lithium chloride curve for the wateralcohol mixtures is the expected one. The reason for the deviation of the curve for hydrochloric acid from linearity is difficult to trace. At present it seems to be somewhat improbable that the hydrogen– or silver–silver chloride electrodes could be in error. Scatchard,[11] who previously noted this behavior of hydrochloric acid, did not succeed in giving a plausible explanation.

Aside from the deviations for hydrochloric acid at high alcohol concentrations, which may be due to purely chemical causes, we thus find the theory of the inverse proportionality of the dielectric constant to the logarithm of the activity coefficient at infinite dilution to be fairly well supported by the experimental evidence. There are two questions that should be considered in relation to this result. Is the value for log γ_{∞} at constant dielectric constant independent of the solvent mixture used and further will the slope of the activity coefficient curves under the same conditions be the same in all cases? Measurements to be found in the literature that might be used for a study of these two points seem to be rather unreliable or in a given case too few and it has not been possible to deduce any definite safe information from them.

Summary

The thermodynamic properties of potassium, sodium and lithium chlorides and hydrochloric acid in water–methyl alcohol mixtures have been measured at 25° with the following cells

Ag/AgCl/MeCl *(m)* in water/Me_yHg/MeCl (*m*) in water-alc./AgCl/Ag
Ag/AgCl/HCl *(m)* in water–alcohol/H_2 (760 mm. partial pressure)

From these measurements were calculated the activity coefficients at the concentrations used, which in turn gave the values at infinite dilution in relation to the corresponding pure water value assumed to be unity.

The connection between the infinity values for the activity coefficients and the composition and dielectric properties of the water–methyl alcohol mixtures has been briefly discussed.

NEW HAVEN, CONNECTICUT

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[11] Scatchard, THIS JOURNAL, 47, 2098 (1925); 49, 217 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXIX. GERMANIUM MONOHYDRIDE[1]

BY L. M. DENNIS AND N. A. SKOW

RECEIVED MARCH 8, 1930 PUBLISHED JUNE 6, 1930

The hydrides of the type RH_4 of carbon, silicon, germanium, tin and lead elements in the fourth group of the Periodic Table are known. Higher homologs of the type R_nH_{2n+2} of carbon, silicon and germanium have also been prepared. Carbon alone of these five elements has yielded hydrides of the type R_nH_{2n}.

Of the hydrides of the type R_nH_n, acetylene is familiar, and analogous hydrides of silicon,[2] tin[3] and lead[4] have been announced, although each deserves further study. Bradley and Weeks give for the three compounds the formulas Si_2H_2, Sn_2H_2 and Pb_2H_2 but, since no determinations of the molecular weights were made, they should for the present be represented by the general formula (RH),.

When an alloy of germanium and magnesium is treated with dilute hydrochloric acid, the chief products[5] are germanium hydrides of the type Ge_nH_{2n+2}.

Haller took up in the Cornell Laboratory some three years ago the study of the product obtained by treating an alloy of calcium and germanium with hydrochloric acid. He obtained a powder which spontaneously dissociated. No detailed study was made of it at that time.

Experimental

With the thought that an alloy of an alkali metal with germanium might yield unsaturated germanium hydrides more readily than a calcium–germanium alloy, a mixture of powdered germanium and small pieces of sodium in equi-atomic proportions was heated to 1000° in a small, special steel crucible provided with a steel cover which made an air-tight seal when bolted into place. When the cooled crucible was opened, it was found to be filled with a dense, hard, pyrophoric product, analysis and microscopic examination of which showed it to be a homogeneous alloy of the composition NaGe. *Anal.* Calcd. for NaGe: Na, **24.06;** Ge, **75.94.** Found: Na, **24.08;** Ge, **75.94.**

Sodium Germanide

The alloy is slowly acted upon by moist air, and consequently it must be kept in a tightly closed receptacle or under a dry, inert gas.

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by N. A. Skow in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Bradley, *Chem. News,* 82, 149 (1900).

[3] Weeks, *Rec.* trav. *chim., 45,* 201 (1926).

[4] Weeks, J. *Chem. Soc.,* 127, 2845 (1925).

[5] Dennis, Corey and Moore, THIS JOURNAL, 46, 657 (1924).

When this sodium germanide was added to cold water, or to dilute or concentrated hydrochloric acid, a dark brown powder was formed.

When this was collected on a filter and washed with water, it decomposed with a puff but without detonation, when dried in the air. When water was removed from it by washing it on the filter first with alcohol and then with ether, it exploded with slight detonation as soon as the ether had run through the funnel.

After somewhat extensive experimentation, the analysis of the product was successfully accomplished in the following manner.

The sodium germanide was carefully ground to a fine powder in a dry agate mortar, and then was added in small portions to cold water to avoid rise of temperature during the reaction. The brown powder was then collected on a filter, washed first with water, then with alcohol and finally with ether, and, keeping it moist with ether, was rinsed with a jet of ether into B of the double U-bulb **A**, Fig. 1, which had previously been weighed while evacuated. The bulb-tube was attached to the chain by the ground joints as shown, and with M closed and R open, pure, dry carbon dioxide was passed over the sample until the ether was removed. D was closed and both B and C were evacuated through the two-way stopcock E, which was then closed. **A** was then detached and weighed. It was afterwards found that the substance slowly dissociates in a vacuum at room temperature, but as the products of the decomposition could not escape from **A**, this partial disintegration had no effect upon the weight of the sample.

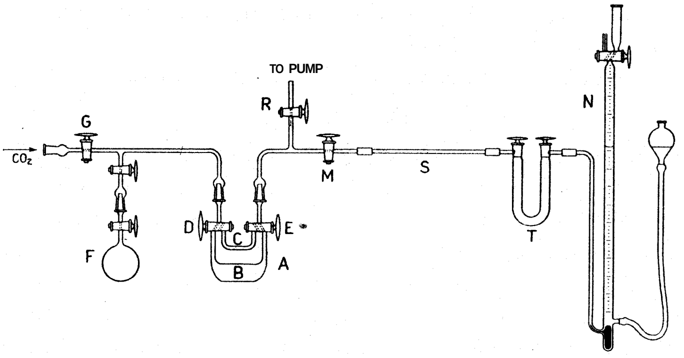

Fig. 1

A was now again attached to the chain, and all air in the connecting tubes and other parts of the apparatus was swept out by passing carbon dioxide through C and the remainder of the chain into the Schiff nitrometer N, which contained a concentrated solution of potassium hydroxide. When complete absorption of the gas in N showed that air had been removed, the stopcocks D and E were closed, and a glycerin-bath was brought up around B, which contained the sample. The bath was heated to 165°, at which temperature the substance dissociated with an explosive puff, filling the bulb with finely divided germanium and liberating hydrogen. The bath was removed, D and E were turned to communicate with B, and carbon dioxide was slowly passed through the bulb, sweeping out all gases through S and T into N. S was a thin-walled tube of quartz which was heated by a gas flame during the passage of the gases: any germanium escaping from B as a hydride was decomposed, depositing germanium on the walls of S, and liberating hydrogen, which passed on into N. T was a U-tube containing pumice and sulfuric acid for absorption of any water that the sample might still have contained.

S and T were now detached and weighed, and A was evacuated and then weighed. The hydrogen in N was measured, and its purity was then ascertained by combustion in a Dennis–Hopkins combustion pipet.

Anal. Subs., 0.1847: found, Ge (in B and S), 0.1699; H, 0.0029; H_2O, 0.0119. Subtracting from the weight of the sample the weight of water found, the results of the analysis were: Subs., 0.1728: Ge, 0.1699; H, 0.0029. Calcd. for $(GeH)_x$: Ge, 0.1699 = 98.63; H, 0.0029 = 1.37. Found: Ge, 0 1699 = 98.63; H, 0.0029 = 1.37. The results of two other analyses, calculated on the dry sample as before, were: ***Anal.*** Subs , 0.1566, 0.1004: Calcd. for $(GeH)_x$: Ge, 0.1544, 0 0990; H, 0.0021, 0 00137. Found: Ge, 0 1543 = 98.53, 0.0990 = 98.63; H, 0 0021 = 1.37; 0.00137 = 1 37.

The analyses show the substance to be germanium monohydride.

Germanium Monohydride

Prepared in the manner above described, the compound is a dark brown powder that decomposes with an explosive puff when dried in the air. In an inert gas or in a vacuum the substance dissociates only very slowly at room temperature, but when warmed to about 165° it suddenly breaks down with a slight detonation, yielding hydrogen and germanium.

Qualitative tests showed that the substance is not soluble without change in any of the usual inorganic or organic solvents. Dilute or concentrated nitric acid rapidly oxidizes the germanium to the dioxide. Concentrated solutions of alkali hydroxides are without action. Hydrogen peroxide readily oxidizes it with solution of the resulting germanium dioxide.

The following experiments were made with samples of the compound that had been freed entirely from moisture; this was accomplished by holding it for two hours at 140° in a current of carbon dioxide. Analysis of the residue showed it to be anhydrous $(GeH)_x$ of high purity.

Hydrogen chloride was without appreciable action upon the germanium monohydride at temperatures below that at which the compound dissociated.

A solution of potassium permanganate acidulated with sulfuric acid quantitatively oxidized the substance.

$$2GeH + 2KMnO_4 + 3H_2SO_4 = 2GeO_2 + K_2SO_4 + 2MnSO_4 + 4H_2O$$

Dry fluorine instantly attacked the compound with a burst of flame and the formation of germanium tetrafluoride and hydrogen fluoride.

The reaction between germanium monohydride and dry chlorine was studied in the following manner. A sample of the hydride was collected and dried in B and both B and C were then evacuated and A was weighed. The amount of chlorine called for by the equation

$$2GeH + 5Cl_2 = 2GeCl_4 + 2HCl$$

was brought into the bulb F, the chlorine was frozen by means of liquid air, and the air in the tube was pumped out through C and R. The refrigerant from around F was then removed, D was opened and chlorine was admitted in small portions into B. The monohydride reacted energetically with chlorine and disappeared when all of the gas had been admitted. If the reaction proceeds according to the equation given above, 0.0606 g. of hydrogen chloride, and 0.3566 g. of $GeCl_4$ should have been formed. The amounts found were 0.0609 g. of hydrogen chloride and 0.3562 g. of $GeCl_4$. The purity of the latter was shown by its vapor tension at 0°, 24.4 mm. The experiment was repeated, introducing smaller amounts of chlorine than were called for in the above equation, to ascertain whether lower chlorides of germanium would be formed. In each case only a portion of the monohydride was acted upon, and only $GeCl_4$ was produced.

The reaction with bromine was similar to that with chlorine, only pure $GeBr_4$ being formed even when the germanium monohydride was present in excess.

Vapor of iodine acted slowly upon the monohydride to form GeI_4.

Summary

When sodium germanide, NaGe, reacts with water, germanium monohydride $(GeH)_x$ is formed. This is a brown solid which instantly dissociates with an explosive puff when the dry, or nearly dry, substance is brought into contact with the air. When in an inert gas or a vacuum the compound dissociates only slowly. The monohydride is a strong reducing agent, and unites with the free halogens to form compounds of the type GeX_4.

The preparation of $(GeH)_x$ completes the series of hydrides of the type R_nH_n in the group carbon to lead.

ITHACA, NEW YORK

[CONTRIBUTION PROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO 247]

THE ELECTRODE POTENTIAL OF INDIUM AGAINST INDIUM CHLORIDE SOLUTIONS

BY SHIN'ICHIRÔ HAKOMORI

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Upon the electrode potential of metallic indium there exist only the early inexact investigations of Erhard* and Thiel.[2] Later, Richards and Wilson[3] determined with great precision the electromotive forces of cells containing indium amalgams of various concentrations, but they did not measure the pure metal in relation to these amalgams.

This investigation was therefore undertaken for the purpose of obtaining accurate values of the electrode potential of metallic indium against solu-

[1] Erhard, *Z. anorg. Chem.*, *39*, 119 (1904).

[2] Thiel, *Wied.* **Ann.**, *14*, 504 (1881).

[3] Richards and Wilson, *Z. physik. Chem.*, *72*, 129 (1910).

tions of its chloride at various concentrations. The solutions were always given a definite concentration (0.02 f.) of hydrochloric acid, so as to eliminate any possible hydrolysis of the salt. For the other electrode silver covered with silver chloride was used. The cells measured were, therefore

$$\text{In(s), InCl}_3(c\text{ f}) + \text{HCl(0.02 f.), AgCl(s)} + \text{Ag(s)}$$

This investigation was undertaken at the suggestion of Professor A. A. Noyes. I desire to express my indebtedness to him and to Professor Don M. Yost of this Tnstitute for many useful suggestions, and to Dr. H. D. Kirschman for the preliminary work which he did on this research.

Substances and Solutions

Purification of the Indium.—A commercial sample of metallic indium was dissolved in aqua regia, the solution was evaporated to dryness, and the evaporation was repeated three times with addition of hydrochloric acid each time, so as to remove all nitric acid. The residue of indium chloride was taken up with water and the indium was precipitated as hydroxide by adding ammonium hydroxide to the hot solution. The precipitation was repeated three times, so as to remove any impurities soluble in excess of ammonia. The indium hydroxide thus obtained was dissolved in hydrochloric acid and the solution was evaporated to sirupy consistency. Then the residue was dissolved in the least quantity of water, and recrystallized ammonium thiocyanate was added. Since a red coloration showed the presence of considerable iron, the solution was extracted with pure ether until no more coloration was produced when fresh thiocyanate was added. This ether extraction would also remove any gallium or thallium possibly present. The indium chloride solution was then electrolyzed, using 5 volts and 0.5 ampere. A thick platinum wire placed in a porous cup served as anode, and a thin platinum wire with only its point dipping into the solution was used as cathode. The spongy indium thereby resulting was washed thoroughly with water, pure alcohol, and ether, and was dried and kept in a desiccator. It was used both for the indium electrode and for the preparation of indium chloride.

Preparation of the Indium Chloride.—The indium (mixed with sugar carbon when the quantity was large) was placed in a porcelain boat and'heated in a pyrex glass tube to a dull red heat in a current of well-dried chlorine gas, which was prepared by adding pure hydrochloric acid to potassium permanganate crystals. After the chlorination was complete, the indium chloride was sublimed at a red heat in a current of nitrogen into a pyrex glass receiver, which was then sealed off. Throughout all these operations moisture was carefully excluded.

Preparation of the Silver and Silver Chloride.—The silver and the silver chloride uoed in the cell were prepared according to the directions of Randall and Young[4] and kept in the dark under water.

Water and Hydrochloric Acid.—All the water used in making the solutions had been redistilled from alkaline permanganate. The hydrochloric acid used was the "C. P. analyzed," stated to contain entirely negligible quantities of impurities.

Analysis of the Indium Solution.—The method of analysis adopted was the potentiometric process developed by Bray and Kirschman.[5] It was found that the precision of the method was increased when the platinum electrode was carefully cleaned before each determination and when ample time was allowed for reaching equilibrium.

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[4] Randall and Young, THIS JOURNAL, 50,990 (1928).

[5] Bray and Kirschrnan, *ibid.*, 49, 2739 (1927).

Apparatus and Procedure

Apparatus.—The electrode vessel was similar to those commonly used in this Laboratory.[6] It contained two indium electrodes and three silver chloride electrodes, thus making it possible to check the constancy of the respective electrodes. The electrode vessel was placed in a water thermostat whose temperature was kept at 25.00 ± 0.02°, as determined by a thermometer which had been compared with one calibrated by the Bureau of Standards.

A Leeds and Northrup Type K potentiometer was used, also a Weston cadmium standard cell of the unsaturated type certified to have an electromotive force of 1.01878 volts.

Procedure.—The spongy indium and the finely divided silver and silver chloride, before they were put into the cell, were washed several times with the solution with which the measurement was to be made. This was found to be essential in obtaining the most concordant results. Potential measurements were made after six hours and after various longer intervals during two days. The potential was found to reach the equilibrium value in twelve hours after the setting up of the cell, and to remain constant within **0.3** mv. for even forty-eight to sixty hours. The values with the three different silver chloride electrodes agreed with one another within 0.2–0.3 mv., and those with the different indium electrodes within 0.4 mv.

In some of the experiments the indium electrode was protected against the influence of dissolved atmospheric oxygen by bubbling a current of purified nitrogen through the indium solution, but this had no effect on the constancy of the potential values. The silver chloride electrode was not protected from the light.

The Observed Electromotive Forces.—The values in millivolts of the electromotive force at various times after the cell was set up are shown in Table I. It will be seen that after six hours there was very little change in the reading. The values after twenty-four hours were adopted as the final ones. The formality of the indium chloride is expressed in formula weights per liter of solution.

TABLE I

THE OBSERVED ELECTROMOTIVE FORCES AT 25°

Soln. no.	Formality of indium chloride	Electromotive force				
		6 hours	12 hours	24 hours	36 hours	48 hours
1	0.001515	735.94	736.96	737.03	....	....
2	.005332	726.60	726.60	726.44	726.31	....
3	.01104	....	....	719.11	719.43	719.41
4	.02744	....	....	706.13	706.14	706.27

Discussion of the Results

The electromotive forces E of the cells above considered should be expressed by the following equations, in which (In^{+++}) and (Cl^-) represent

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[6] U. B. Bray, THIS JOURNAL, 49, 2372 (1927).

the molal concentrations, α_{In} and α_{Cl} are the activity coefficients (hereafter called the ***activations)*** of the two ions in the solution involved, and $\bar{E}_{In}$ and $\bar{E}_{AgCl}$ are the molal potentials of the two electrodes

$$E = \bar{E}_{In} - \bar{E}_{AgCl} - 0.01972 \log_{10} (In^{+++})(Cl^-)^3\alpha_{In}\alpha^3_{Cl} \qquad (1)$$

Or, introducing a new symbol E' and putting $\bar{E}_{In} - \bar{E}_{AgCl} = E'_0$, we get:

$$E + 0.01972 \log_{10} (In^{+++})(Cl^-)^3 = E' = E'_0 - 0.01972 \log_{10} \alpha_{In}\alpha^3_{Cl} \qquad (2)$$

Hence if the four known values of the first member of this equation are plotted against a simple function (such as the square root) of the concentration of indium chloride in the respective experiments, and if the graph is extrapolated for an indium-ion concentration of zero (and hence for a hydrochloric acid concentration of 0.02 formal), there will be obtained the electromotive force $E'_{0.02}$ of a hypothetical cell with electrodes of indium and silver chloride containing the ions In^{+++} and Cl^- each at 1 molal, but having such activations α_{In} and α_{Cl} as these ions would have in a solution 0.02 M in H^+ and 0.02 *M* in Cl^- containing no other ions. Another graphical determination of this quantity $E'_{0.02}$ may be made by plotting the first member of Equation 2 against the square root, $\sqrt{\frac{1}{2}\Sigma(cz^2)}$, of the ionic strength of the solution, and reading off the extrapolated value corresponding to an ionic strength of 0.02 molal.

Table II shows the results of the computations and the data used for constructing the plots.

TABLE II

COMPUTATIONS BASED UPON THE OBSERVED ELECTROMOTIVE FORCES

Expt. no.	Concentrations (In^{+++})	(Cl^-)	$\frac{1}{2}\Sigma(cz^2)$	Electromotive force E (obs.)	E' (calcd)	Activation product, $\alpha_{In}\alpha^3_{Cl}$ Expt.	Theory
1	0 02744	0 1023	0 1846	0 7061	0.6167	0 00106	0.0025
2	.01104	.05312	0862	,7191	.6051	.0041	.0165
3	.00533	.03600	.0520	.7264	.5962	.0116	.0417
4	.001515	.02425	,0291	.7370	.5861	.0376	.0925
From plots	.00	.02000	.02000	...	.575	(.139)	0.139
By extrap.	.00	.00	.00	...	558	1.00	1.00

The values of $E'_{0.02}$ (that is, of E' in 0.02 f. HCl), obtained by extrapolating the graphs, are 0.574 and 0.578, respectively, thus in fair agreement with each other. Adopting 0.575 as the best value of $E'_{0.02}$, the value of E'_0 at zero concentration (which is equal to the difference $\bar{E}_{In} - \bar{E}_{AgCl}$ of the two molal electrode potentials) can be found with the aid of the last part of Equation 2 by taking the value[7] of α_{Cl} equal to 0.848 and that of ***a,,*** equal to 0.228 as found by the equation,[8] $\log_{10} a = -0.357\, z^2 \sqrt{\Sigma cz^2} = -0.357$

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[7] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 382, derived experimentally the value 0.89. It might be somewhat more exact to employ this value; **but** its use increases the calculated value of E'_0 only inappreciably (from 0.558 to 0.559).

[8] Noyes, THIS JOURNAL, 46, 1099 (1924).

$\times 9 \times \sqrt{0.04}$ derived from the ion attraction theory of Debye and Hückel for very dilute aqueous solutions at 25°. A value of E_0' (at zero concentration) might also be found by extrapolating the graph to an ionic strength of zero, but the long extrapolation involved is so uncertain as to make the result of no value.

The value of E_0' so derived is **0.558** volt. Adding to this the molal electrode potential (—0.222 volt)[9] of Ag + AgCl, Cl^-, there is obtained for the molal electrode potential of In, In^{+++} the value 0.336 volt, referred to the molal hydrogen electrode.

By means of Equation 2 values of the activation product $\alpha_{In}\alpha_{Cl}^3$ in the various solutions were calculated from the values of E' and E_0'. These are recorded in the next to last column of the table. In the last column of the table are given the values of this product calculated by the following equation derived from the ion-attraction theory for very dilute solutions of a completely ionized salt of the type $InCl_3$ at 25°.

$$-\log_{10} \alpha_{In}\alpha_{Cl}^3 = 12 \times 0.357 \sqrt{\Sigma cz^2}$$

The activation product derived from the electromotive forces will be seen to decrease with increasing concentration much more rapidly than do the theoretical values derived from the dilute solution formula of the ion-attraction theory. This is the opposite of what usually occurs. It may arise from the existence of the salt in the un-ionized form, or from the formation of complex ions (such as $InCl_4^-$), in considerable quantity in the more concentrated solutions.

Summary

In this article there have been described precise measurements of the electromotive forces at 25° of cells of the type In(s), $InCl_3(c)$ + HCl (0.02 f.), AgCl(s) + Ag(s) with the molal concentration c ranging from 0.0015 to 0.0274. From the observations, by graphic extrapolation and by applying the ion-attraction theory to the results at the smallest concentration, the electromotive force of the cell In(s), In^{+++} (1 m.) || Cl^- (1 M), AgCl(s) + Ag(s) (where the molalities represent ion activities) was found to be **0.558** volt. Adding to this the potential (—0.222 volt) of Ag + AgCl, Cl^-(1 M), the molal electrode potential of In(s), In^{+++} becomes +0.336 volt referred to the molal hydrogen electrode. This places indium in the electromotive series very near thallium (0.336 against Tl^+ ion), and between cadmium (0.397) and tin (0.13) or lead (0.12).

PASADENA, CALIFORNIA

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[9] Randall and Young, THIS JOURNAL, 50, 989 (1928).

[Contribution from the Frick Chemical Laboratory, Princeton University]

THE MECHANISM OF THE PHOTOCHEMICAL DECOMPOSITION OF OZONE

By Hans Joachim Schumacher[1]

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Introduction

Investigations concerning the photochemical decomposition of ozone have been presented by Regener,[2] E. v. Bahr,[3] Warburg,[4] Weigert,[5] Weigert and Böhm,[6] Griffith and Shutt,[7] Griffith and McWillie[8] and Kistiakowsky.[9] The results of their researches have been summarized by Kistiakowsky[9] and by Griffith and McKeown;[10] nevertheless, it is necessary to restate briefly the experimental facts before proceeding to a discussion of the mechanism.

Regener[2] has investigated the equilibrium of formation and decomposition of ozone in different regions of the ultraviolet light. The light source was an aluminum arc from which in one series of experiments all light of wave lengths $\lambda < 2100$ Å. was filtered out by a plate of calcite. As he was not particularly interested in the kinetics of the reaction, his velocity measurements are incomplete and only roughly quantitative. Nevertheless, it can be estimated that for constant light absorption the velocity of decomposition is nearly proportional to the ozone concentration. It is important to note that a positive temperature coefficient for the decomposition of ozone was obtained at total pressures of 1 atm., of which about 1–5% was ozone and the rest oxygen.

E. v. Bahr[3] has worked with highly dilute mixtures of ozone, the pressure of which was usually of the order of 1 mm. of mercury or less. The total radiation of a mercury lamp was used and the ozone concentration determined by optical measurements. Her data can be used only qualitatively because experiments of the same kind deviate from each other by about 100% due to neglect of a dark reaction, and the inaccurate method of analysis. Nevertheless, her results are important. E. v. Bahr finds that the quantum yield increases very markedly with decreasing pressure. (She measured only the velocity of the reaction, but the quantum yield and velocity

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[1] International Research Fellow.

[2] Regener, *Ann. Physik*, **20**, 1033 (1906).

[3] E. v. Bahr, *ibid.*, *33*, 589 (1910).

[4] Warburg, *Sitzb. preuss. Akad. Wiss.*, 644 (1913).

[5] Weigert, *Z. physik. Chem.*, **80**, *87* (1912).

[6] Weigert and Böhm, *ibid.*, **90**, 233 (1915).

[7] Griffith and Shutt, *J. Chem. Soc.*, **123**, 2752 (1923).

[8] Griffith and McWillie, *ibid.*, **123**, 2762 (1923).

[9] G. B. Kistiakowsky, *Z. physik. Chem.*, **117**, 337 (1925).

[10] Griffith and McKeown, "Photoprocesses in Gaseous and Liquid Systems," Longmans, Greene and Co., London, **1929.**

under the same conditions are, of course, proportional to each other.) At a total pressure of 20 mm. of mercury the reaction is ten to twenty times more rapid than at one atmosphere.

Weigert[5] has also investigated the decomposition of ozone in the ultraviolet, his light source being a mercury arc. The total pressure was always one atmosphere and the concentration of ozone varied from 0.9–6%. He found that when all light was absorbed, the order of the reaction was about one, whereas when the concentration of ozone was small, so that the light was not completely absorbed, the order of the reaction increased.

Weigert and Böhm[6] also studied the influence of hydrogen on the reaction and observed that the velocity of the decomposition of ozone was greatly increased. In the presence of a large excess of hydrogen the reaction rate was changed five- to ten-fold and water was formed.

Griffith[7] and co-workers have studied the decomposition of ozone in the visible range in the presence of oxygen and foreign gases at total pressures of 1 atm. When the oxygen was replaced by helium, nitrogen or carbon dioxide the velocity increased in the order $O_2 \longrightarrow N_2 \longrightarrow CO_2 \longrightarrow$ He. Kistiakowsky[8] has shown that all gases inhibit the reaction, the inhibiting influence decreasing in the order given.

Hydrogen, according to Griffith, shows qualitatively the same influence on the reaction in the visible that Griffith and Bohm found in ultraviolet light, *i. e.*, the rate of decomposition of ozone increases and water is formed.

Heretofore these results were not of much use in the development of theories to explain the reaction because monochromatic light was not used, quantum efficiencies were not determined and the other experimental conditions were not varied sufficiently. Kistiakowsky[8] has given an empirical equation for the representation of some of these results.

Quantum yields for the decomposition of ozone in monochromatic light have been determined by Warburg[4] in the ultraviolet and by Kistiakowsky[8] in the red region. The important result of Warburg's work is that at a total pressure of 1 atm. and a partial pressure of a few mm. of ozone, the quantum efficiency is, with oxygen as added gas, about 0.30 mol. $O_3/h\nu$, with nitrogen 1.09 and with helium 1.70.

Most of the experimental facts upon which the following theoretical considerations are based are found in the work of Kistiakowsky: for he varied the total pressure as well as the concentrations of the gases over a wide range and, which is more important, in his experiments the thermal decomposition of ozone was eliminated or could be estimated approximately. The velocity obtained by Warburg[4] in ultraviolet light always included a dark reaction whose rate was not determined and, as will be shown later, this is of particular importance in explaining some of his results.

The Decomposition of Ozone in Red Light.—To express the experimental data obtained in red light, Kistiakowsky has given the empirical eauation

$$-\frac{d[O_3]}{dt} = \frac{k\,I_{abs.}\,[O_3]^{1/2}}{m[X] + [O_2]}$$

in which X denotes the concentration of the added gas and m a factor less than one. The equation is valid over only a limited range of pressure and concentration; at low total pressures, for example, the velocity is nearly proportional to $I_{abs.}$. Later unpublished experiments of Kistiakowsky,[11] which represent the course of the reaction in a more satisfactory manner because of better energy measurements and the more accurate determination of the final ozone concentration, show still more pronouncedly that the given equation can be used over only a limited range. On the other hand, since it is impossible to represent the reaction by a simple equation, it must be assumed that this can be done only by an equation of several terms.

It is characteristic of the decomposition in red light that the quantum yield, even at high ozone concentration, is relatively small. The greatest values of the quantum yield are between 2 and **3** moles $O_3/h\nu$ and are obtained at relatively low total pressures and high ozone concentration.[12] At high total pressures the quantum yield decreases and at **1** atm. pressure with 50% ozone it is less than unity (Experiment 3).[12]

At total pressures below 10 mm. the quantum yield is nearly 2. In the presence of 1–2 mm. of oxygen and 8–9 mm. of ozone it is about 2.5 and in the presence of 8–9 mm. of oxygen and 1–2 mm. of ozone it is about 1.5 (unpublished experiments of Kistiakowsky). It must be emphasized that greater velocities can also be obtained at higher total pressures if oxygen is replaced by foreign gases. According to Kistiakowsky, on the basis of oxygen equal to 1, the inhibiting action of helium is represented by 0.13, nitrogen 0.3 and carbon dioxide 0.8. The essential facts already given should readily follow from the mechanism of the reaction.[13]

It is of considerable importance to know whether to assume for the primary reaction the formation of an excited molecule of ozone or an atom of oxygen. Before treating the energy relations and the ozone spectrum we shall see which of the two possibilities should be selected from the ki-

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[11] These experiments were carried out in 1925 by Dr. Kistiakowsky in the Kaiser Wilhelm Institut für Physikalische Chemie in Berlin, but could not be interpreted *at* that time and therefore were not published.

[12] Kistiakowsky, *Z. physik. Chem.*, **117**, *348 (1925).*

[13] In this treatment a chain will be regarded as formed when more than **2** molecules of ozone react per quantum absorbed. We shall find that the measured quantum yield is not necessarily identical with the number of ozone molecules which react per quantum absorbed because ozone may also be regenerated. In spite of this difference the experimentally determined quantum yield, whose usual value is considerably less than 2, shows that there are often no chains or only a few short ones. Consequently, we can neglect chain formation without seriously limiting the validity of the theoretical treatment.

netics of the reaction. If we assume for the primary reaction the formation of an excited ozone molecule

$$O_3 + h\nu \longrightarrow O_3' \qquad (1)$$

we have only a limited number of possible reactions that may follow, namely

$$O_3' + O_3 \longrightarrow 3O_2^* \qquad (2)$$
$$O_3' + O_3 \longrightarrow 2O_3 \qquad (3)$$
$$O_3' + O_2 \longrightarrow O_3 + O_2 \qquad (4)$$

Reaction 2 may start a chain if we assume that the energy-rich oxygen molecule (O_2^*) can excite an ozone molecule. For reasons previously given we shall, however, neglect the formation of chains. Reactions 3 and 4 indicate the deactivating influence of the two gases. From this mechanism the following equation is derived

$$-\frac{d[O_3]}{dt} = \frac{I_{\text{abs.}}\,[O_3]}{(k_2 + k_3)[O_3] + k_4[O_2]}$$

If a foreign gas X is present, another term $k_5[X]$ is added to the denominator. From this equation it is evident that the total pressure should have no influence. If the oxygen–ozone ratio is constant, the quantum yield should be independent of the pressure. This is contrary to the experimental facts and, since on the assumption of excited molecules there are no other possible reactions than those already given, the formation of excited ozone molecules in the investigations previously discussed must be rejected. Thus we see that kinetic considerations lead us to assume the formation of oxygen atoms in the primary reaction.

We shall now consider the energy relations involved. The work of G. Herzberg[14] and R. Mecke[15] shows that the heat of dissociation of oxygen is below 6 volts; the value given by Mecke is 128,000 cal. per mole. The heat of decomposition of ozone is 32,000 cal. per mole. The minimum energy required by the reaction

$$O_3 \longrightarrow O_2 + O$$

is, therefore, only $(128{,}000/2) - 32{,}000 = 32{,}000$ cal., while the energy of the red light is more than 40,000 cal. (In the experiments of Kistiakowsky the mean absorption was at 6200 Å.) Of course, absorption of light of greater energy than the heat of dissociation does not necessarily require the dissociation of the molecule. This depends on the nature of the spectrum, as was first shown by Franck and his co-workers.

The ozone spectrum[16] consists of very diffuse bands in the red so that we may assume that predissociation[17,18] occurs even at these wave lengths.

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[14] G. Herzberg, *Z physik. Chem.*, **4B,** 223 (1929).

[15] R. Mecke, *Naturwissenschaften*, **51,** 596 (1929).

[16] Private communication from Dr. O. R. Wulf, who is now investigating the ozone spectrum.

[17] V. Henri, *Nature,* December 20, 1924; *Trans. Faraday Soc*, **25, 765** (1929).

[18] Bonhoeffer and Farkas, Z. *physik. Chem.,* **132,** 235 (1928).

These considerations show that the reaction

$$O_3 + h\nu \longrightarrow O_2 + O$$

is quite probable. Neglecting the formation of chains, only the following reactions are possible

$$O_3 + h\nu \longrightarrow O_2 + O \tag{1}$$
$$O + O_3 \longrightarrow 2O_2^* \tag{2}$$
$$O + O_2 + M \longrightarrow O_3 + M \tag{3}$$

Reaction 2 can lead to chain formation. Equation **3** is a three-body reaction where M designates the third body. In the presence of little ozone and much oxygen, the oxygen pressure may be regarded as equivalent to M. If oxygen is replaced by helium, nitrogen or any other gas, M is represented by the pressure of this gas. In polyatomic gases a first approximation for M is given by the total pressure of the mixture, since ozone has influence also. The effect of various gases is specific, due to their difference in structure and specific ability to take up internal energy by collision; but polyatomic molecules are nearly the same in this respect and differ from each other generally by a factor less than **3.**

From the preceding mechanism the following equation is derived

$$-\frac{d[O_3]}{dt} = I_{abs.} + k_2[O][O_3] - k_3[O][O_2][M]$$

$$[O] = \frac{I_{abs.}}{k_2[O_3] + k_3[O_2][M]}$$

$$-\frac{d[O_3]}{dt} = I_{abs.}\left[1 + \frac{k_2[O_3]}{k_2[O_3] + k_3[O_2][M]} - \frac{k_3[O_2][M]}{k_2[O_3] + k_3[O_2][M]}\right] \tag{I}$$

Equation I should represent the experimental facts previously mentioned. It can be regarded as a first approximation since chain formation has been neglected.

Of course, Equation I can be written

$$-\frac{d[O_3]}{dt} = I_{abs.}\left(\frac{2k_2[O_3]}{k_2[O_3] + k_3[O_2][M]}\right) \tag{II}$$

Since Equation I illustrates the mechanism better, it will be used in the following discussion.

When the ozone concentration is small and is held constant, *e.* g. $[O_3] <$ **10** mm. of mercury, and the total pressure is decreased (which means also decreasing the oxygen pressure), the third term of the equation becomes smaller and smaller and the second term approaches unity. For the limit we have

$$-\frac{d[O_3]}{dt} = I_{abs.}\ [1 + 1] \quad \text{or}$$

$$\frac{-\frac{d[O_3]}{dt}}{I_{abs.}} = 2 \text{ (Quantum Yield)} \tag{III}$$

This case corresponds to Expts. 11 and 12 in the paper of Kistiakowsky (p. **149).** The equation **(I)** shows that in this region the quantum yield is strongly influenced by pressure. With a small increase of $[O_2]$ and $[M]$ the negative term can no longer be neglected. Experiments 10 and 12 of Kistiakowsky illustrate this point; some of his unpublished experiments bring it out still more clearly. Furthermore, the experiments show that at low total pressures and very small concentrations of oxygen the quantum yield is greater than 2. This is to be expected from the proposed mechanism for under these conditions chain formation according to Reaction 2 is strongly favored. In the presence of more oxygen the activated molecules may be deactivated, so the probability of forming a chain is decreased.

Let us now consider a high total pressure and a small concentration of ozone. In this case we have

$$k_2[O_3] < k_3[O_2][M]$$

Then the equation becomes

$$-\frac{d[O_3]}{dt} = \frac{2\,I_{abs.}\,k_2[O_3]}{k_3[O_2][M]} \tag{IV}$$

In consequence of the small $[O_3]$, the total pressure and the oxygen concentration can change only to a slight extent during the reaction, which means that the denominator of Equation IV becomes constant and the rate of ozone decomposition can be given by the simple equation

$$-\frac{d[O_3]}{dt} = k\,I_{abs.}\,[O_3]$$

This case was realized in the work of Griffith and Shutt, who found that at total pressures of one atmosphere and small ozone pressures the reaction follows the equation

$$-\frac{d[O_3]}{dt} = k[O_3]^2$$

In their experiments the light absorption was proportional to the ozone concentration; hence these two equations become identical. Griffith and Shutt found at higher ozone concentration (above 5%) a decrease in the order of the reaction, which is a necessary consequence of Equations I and II. The two other limiting cases are those in which the total pressure and ozone concentration are both large or both small. In the former case with ozone concentration above 90%, a quantum yield greater than 2 should be found. At high pressure the greatest ozone concentration used was about 60% and here, as can be predicted, the quantum yield was considerably less than 2.[19] In the experiments with total pressures below 10 mm. of mercury, the quantum yield becomes much less than 2 if the ratio of oxygen to ozone is greater than five.[20]

If middle values for the oxygen and ozone pressures are employed instead of the extreme concentrations in the cases discussed above, then for con-

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[19] Kistiakowsky, Ref. 9, p. 345, Expts. 2, 3 and 5.

[20] Kistiakowsky, Ref. 9, p. 349, Expts. 10, 11, 12. The unpublished data show that the quantum yield is about 20% too low.

stant light absorption it is to be expected from Formula I or II that the dependence of the velocity on the ozone concentration will vary as $[O_3]^0$ to $[O_3]^1$. As can be readily seen from Equation II, inhibition by oxygen is nearly proportional to its concentration, for the total pressure [M] is $[O_3 + O_2]$ and so, as a first approximation, the whole denominator is proportional to $[O_2]^1$. Therefore we get

$$-\frac{d[O_3]}{dt} = k\frac{I_{abs.}\,[O_3]^{1/2}}{[O_2]}$$

which is identical with the empirical equation of Kistiakowsky.

As is shown by his unpublished work, the limits within which the equation holds are smaller than originally stated by Kistiakowsky. This is in agreement with our deduction of the above equation as a zero approximation.

There are difficulties involved in obtaining the exact mathematical representation of the velocity of decomposition of ozone over the whole range of pressures, for we know only little about the formation of the chains and the deactivation of the energy-rich oxygen molecules by ozone and oxygen. Furthermore, the value of the constant k_3 changes with the composition of the mixture. However, the course of the reaction is essentially represented by Equations I or II and the ratio of the velocity constants of Reactions 2, $O + O_3 \longrightarrow 202$, and 3, $O + O_2 + M \longrightarrow O_3 + M$, can be calculated. The reaction $O + O_2 \longrightarrow O_3$, which requires a three-body collision, occurs at every 10^3 to 10^4 collision at atmospheric pressure, if we assume that no heat of activation is necessary and the third body is well adapted for taking up the excess energy. Then we have[20a]

$$k_3 - \frac{1}{10^3 \times 760}$$

if the total pressure is given in mm. of mercury (in place of 10^3, 10^4 may be used). If ozone and oxygen are well adapted for taking up the excess energy, the above value of k_3 may be used in our general equation. That oxygen is capable of so doing is shown by experiments on the quenching of fluorescence,[21,22] for which oxygen is especially efficient. Likewise, from observations on the prevention of explosions in mixtures of bromine and ozone[Z3] by oxygen we must conclude that the oxygen molecule is extraordinarily able to take up and dissipate the heat of reaction.

From Equation II we get for k_2

$$k_2 = \frac{[O_2][M]\,E}{760 \times 10^3 \times (2 - E)[O_3]}$$

[20a] In the following discussion k_2 and k_3 are the ratio of the velocity constants *to* the number of two-body collisions, that is, k_2 and k_3 give the probability that reaction occurs on collision.

[21] Wood, "Physical Optics," The Macmillan Company, 1923, p. 581.

[22] Norrish, *J. Chem. Soc.*, 1604, 1611 (1929).

[23] Lewis and Schumacher, *Z. Elektrochem.*, 35, **348** (1929); *Z. physik. Chem.*, **6B**, **423** (1930).

where E = $(-d[O_3]/dt)/I_{abs.}$, which is the experimentally determined quantum yield. The values for k_2 in the following experiments have been calculated by means of the above equation.

TABLE I

EXPERIMENTS OF KISTIAKOWSKY"

E = Quantum yield. The pressures of O_3 and O_2 are given in mm. of mercury

Expt. 2

O_3	O_2	P_{total}	E	k_2 X 10^3	
271	215	486	1 06	0 58	
257	236	493	0 89	.50	
209	308	517	.73	64	
167	371	538	47	.48	k mean = 5.4 X 10^{-4}
153	392	545	44	51	
132	423	555	.36	51	
51	544	595	.17	.70	

Expt. 4

167	90	257	1.5	0.55	
144	125	269	1 3	.58	
131	144	275	1 2	.59	
98	193	291	0 81	60	
60	250	310	.51	58	k mean = 5.8 X 10^{-4}
57	255	312	.44	.52	
27	300	327	.30	49	
23	306	329	.23	.68	
20	311	331	.19	.67	

Expt. 5

139	95	234			
133	104	237	1 4	0 63	
126	114	240	1 2	43	
112 5	135	247 5	1 05	43	
78	185	263	0.71	45	k mean = 4.6 X 10^{-4}
55	221	276	.45	47	

UNPUBLISHED EXPERIMENTS OF KISTIAKOWSKY

Expt. 1

O_3	O_2	P_{total}	E	k_2 X 10^3
326	144	470		
317	158	475	1 4	[0 68]
295	191	486	1 2	54
288	202	490	1 1	53
281	213	494	1 0	47
273	225	498	0 9	43
256	249	505	.8	.40
247	262	509	7	37
220	303	523	.6	.35
180	363	543	43	36
160	393	553	40	40
145	415	560	33	41
133	432	565	30	40

TABLE I *(Continued)*

O_3	O_2	P_{total}	E	$k_2 \times 10^3$	
113	462	575	0 29	0 48	
101	480	581	.25	.47	
89	498	587	22	49	
80	512	592	21	54	
55	550	605	14	.46	k mean = 4.5 X 10^{-4}

Expt. 2

O_3	O_2	P_{total}	E	$k_2 \times 10^3$	
212	102	314			
204	114	318	1 4	0 50	
199	122	321	1 3	.46	
189	137	326	1 22	45	
186	141	327	1.10	39	
175	158	333	1.00	.36	
166	171	337	0 95	.38	
155	188	343	85	37	
151	194	345	.75	34	
142	207	349	.70	34	
133	220	353	65	.35	
124	234	358	60	36	
92	282	374	45	33	
80	300	380	35	36	
61	328	387	.29	38	
51	343	394	26	46	
50	345	395	.25	.50	k mean = 4.0 X 10^{-4}

Expt. 4

O_3	O_2	P_{total}	E	$k_2 \times 10^3$	
141	92	233			
138	96	234	1 40	0.48	
127	112	239	1 30	45	
122	119	241	1 20	44	
118	125	243	1 10	.43	
110	137	247	1 00	.37	
106	143	249	0 88	35	
102	149	251	82	32	
97	157	254	.77	.32	
91	166	257	73	33	
86	174	260	67	.33	
81	181	262	67	.37	
77	187	264	.57	32	
74	191	265	.51	30	
67	202	269	49	31	
64	206	270	.47	36	
61	211	272	44	33	
59	214	273	42	34	
57	217	274	41	34	
44	236	280	33	36	
37.5	247	2845	31	40	
36	249	285	29	43	
27	265	292	22	36	
25	268	293	,22	46	k mean = 3.7 × 10^{-4}

TABLE I *(Concluded)*

O1	O_2	P_{total}	E	k_2 X 10^3	
			Expt. 6		
329	207	536			
315	228	543	1.1	0.58	
307	240	547	1.0	.54	
295	258	553	0.9	.49	
282	278	560	.8	.45	
259	309	567	.7	.43	
240	337	577	.6	.42	
229	354	583	.57	.45	
210	380	590	.50	.43	
195	402	597	.50	.50	
181	423	604	.43	.45	
174	434	608	.40	.48	
141	486	627	.25	.50	
128	506	634	.30	.54	
123	513	636	.27	.53	
97	552	649	.20	.44	
93	558	651	.21	.58	
90	562	652	.17	.48	
79	579	658	.16	.51	k mean = 5.0×10^{-4}
			Expt. 7		
90	70	160			
88	73	161	1.4	0.40	
84	79	163	1.3	.35	
78	88	166	1.2	.34	
70	100	170	1.0	.28	
67	104	171	0.95	.31	
61	113	174	.90	.32	
59	116	175	.86	.32	
54	124	178	.76	.30	
51	128	179	.73	.32	
49	131	180	.69	.32	
47	134	187	.70	.35	
45	137	182	.66	.35	
44	139	183	.65	.36	
32.5	156	183.5	.55	.36	
31	159	190	.55	.47	
29.5	161	191.5	.49	.43	k mean = 3.5×10^{-4}

[a] *Z. physik. Chem.*, 117, 345 (1925).

It is to be seen that the values of k_2 are fairly constant when $E < 1.5$. Higher values of E indicate the formation of chains and in this region our equation is no longer correct. Furthermore, k_2 gradually increases toward the end of the experiment, which is to be accounted for by the fact that k_3 is assumed to be constant, whereas it really changes with the composition of the mixture. When it is considered that for the calculation of k_2 the quantum efficiency E has been used, and that the error in E is about 10 to

20%, it is realized that the constancy of k_2 is very good. For high values of E (E near 2), large deviations in k_2 are to be expected, because in the equation we have as a factor the difference $(2-E)$. The mean value for k_2 in Expts. 2, 4 and 5 is $[(5.7 + 5.8 + 4.6)/3]\,10^{-4} = 5.4 \times 10^{-4}$; in Expts. 1, 3, 4, 6 and 7, $(4.5 + 4.0 + 3.7 + 5.0 + 3.5)/5 = 4.2 \times 10^{-4}$. In the two cases different light sources were used, which may easily account for the difference in the mean values of k_2. The intensity measurements were more accurate in the unpublished experiments. We have, therefore, to assume for k_2 about 5×10^{-4}, which means that the reaction $O + O_3 \longrightarrow 2O_2$, in which O is a normal atom, occurs only on every 2000th collision. We have the important result that a highly exothermic "Elementarreaktion" does not take place on every collision.[24] Recently two other similar cases have been pointed out by Kistiakowsky.[25] The probability of the occurrence of the reactions $Cl + H_2 \longrightarrow HCl + H$ and $O + H_2 \longrightarrow OH + H$ is also less than 10^{-3}.

The Influence of Foreign Gases.—When oxygen is replaced by foreign gases which do not react with ozone, the quantum efficiency is always greater than that obtained with oxygen. The influence of helium is extraordinarily remarkable, for its inhibiting effect is only $^1/_8$ that of oxygen. From the experiments of Jost[26] it is found that the recombination of bromine atoms is only slightly favored by helium. Hence, it may be readily assumed that also in the case of ozone the effect of helium is given by its influence on the efficiency of the three-body reaction $O + O_2 \longrightarrow O_3$. If helium is the third body the efficiency of the reaction may be one order of magnitude less than with oxygen. The effect of the other foreign gases may depend upon the same phenomenon. Recently it has been shown that the recombination of chlorine atoms[27] is less favored by nitrogen than by oxygen, and similarly in the case of ozone the effect of nitrogen is noticeably less than that of oxygen.

Another argument for the correctness of the idea developed is found in a comparison of the light reaction with the thermal[28] reaction. For the dark reaction the primary process is

$$O_3' + O_3 \longrightarrow 3O_2$$

where O_3' represents a thermally excited ozone molecule. The heat of activation of the thermal reaction is about 28,000 cal. If we assume that there are also excited ozone molecules in the photochemical reaction, then we should expect that foreign gases in both cases would have the same

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[24] H. Beutler and M. Polanyi, *Z. physik. Chem.*, **1B**, 1 (1925).

[25] G. B. Kistiakowsky, THIS JOURNAL, 52, 1868 (1930). See also H. J. Schumacher, forthcoming article in *Z. physik. Chem.*, Abt. *B*.

[26] Jost, *ibid.*, 3B, 95 (1929).

[27] M. Bodenstein, H. J. Schumacher and G. Stieger, *ibid.*, **6B**, in press.

[28] H. J. Schumacher and G. Sprenger, *ibid.*, **6B**, 447 (1930).

effect. However, just the contrary is found. In the thermal reaction all foreign gases accelerate the decomposition, the velocity increasing with increased pressure of the added gas. The acceleration is the smallest for helium. In the light reaction, as previously indicated, it is quite different. All foreign gases inhibit the reaction, the velocity of which decreases in proportion to the amount of the added gas. The inhibiting effect of helium is the smallest. Compared with the oxygen experiments the velocity increases because the inhibiting influence of oxygen is extraordinarily large. By the assumption that in the photochemical reaction oxygen atoms are formed whereas the thermal reaction involves excited molecules, the different behavior in the two cases can be satisfactorily explained.[28]

The Reaction with Hydrogen.—The thermal reaction is only slightly influenced by hydrogen, while in the photochemical reaction, in the red as well as in the ultraviolet, the rate is greatly increased and water is formed.[29] The difference in behavior with respect to hydrogen in the thermal and photochemical reactions may be explained by assuming that excited ozone molecules do not react with hydrogen whereas oxygen atoms react.[30] Yet the reaction $O + H_2 \longrightarrow OH + H$, where O is a normal oxygen atom, occurs only very seldom as was shown by the experiments of Kistiakowsky and my own observations.[31] However, it may be assumed that water is formed according to the reaction $O + O_2 + H_2 \longrightarrow H_2O + O_2$, which is in agreement with the experiments of Weigert, and Griffith and Shutt. They found that in the presence of much hydrogen the rate of water formation becomes constant and practically all of the oxygen formed by the decomposition of ozone is transformed into water. We may have, therefore, for the predominant reactions

$$O_3 + h\nu \longrightarrow O_2 + O \qquad (1)$$

$$O + O_2 + H_2 \longrightarrow H_2O + O_2 \qquad (2)$$

The decomposition of ozone is strongly decreased by Reaction 2, since the reaction $O + O_2 + M \longrightarrow O_3 + M$, which regenerates ozone, is suppressed. The quantum efficiency in the investigated region in the absence of hydrogen is very small, hence a ten-fold increase in the velocity by hydrogen is not surprising. In the ultraviolet, where excited oxygen atoms are formed, the reaction $O + H_2 \longrightarrow OH + H$ may also occur." Our present knowledge of the reactions $O + H_2$ and $O_2 + H_2$, however, is not sufficient to give with certainty the real mechanism of water formation.

The Effect of Temperature.—According to the proposed mechanism there should be no or only a very small temperature coefficient at low pressures where three-body collisions (Reaction 3) would seldom occur and

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[29] Griffith and **Shutt,** J. *Chem. Soc.*, *123*, 2572 (1923); Weigert, *Z. physik. Chem.*, **90, 223** (1915).

[30] Parkas, Goldfinger and Haber, *Naturwissenschaften*, 17, 674 *(1929).*

[31] H. J. Schumachcr, forthcoming article in *Z. physik. Chem* , *(1930).*

where the oxygen atoms, therefore, would always have an opportunity for reacting with ozone molecules. At higher pressures, however, a small but larger temperature coefficient should be found, because the reaction $O + O_2 + M \longrightarrow O_3 + M$ is practically independent of temperature, while the reaction $O + O_3 \longrightarrow 2O_2$ must be influenced by temperature. The unpublished experiments of Kistiakowsky show an increase of the temperature coefficient in the expected direction. (As was pointed out in the introduction, a small positive temperature coefficient at high pressures was also found by Regener.)

In conclusion, it may be said that the decomposition of ozone in red light is satisfactorily represented by the mechanism given.

The Decomposition **of** Ozone in Ultraviolet.—An exact interpretation of the decomposition of ozone in ultraviolet light is rather difficult because of the scarcity of quantitative data. Kistiakowsky has already pointed out the analogy between the reactions in red and ultraviolet light. There are only two important differences: (I) the higher quantum efficiency in the ultraviolet—the only available experiments are with small concentrations of ozone at atmospheric pressure and here the quantum yield is ten times that obtained in red light under the same conditions; *(2)* the influence of water vapor. According to Warburg[4] the decomposition of ozone is more rapid in the presence of moisture, whereas Kistiakowsky, in the red, observed no difference in behavior of dry or wet gases. By analogy with the reaction in the red and because of the fact that the absorption spectrum contains very diffuse bands, we may assume that the primary process in the ultraviolet is also $O_3 + h\nu \longrightarrow O_2 + O$. The acceleration of the reaction rate by a decrease in pressure, observed by E. v. Bahr,[3] may then be readily explained. At low pressures the reaction $O_2 + O + M \longrightarrow O_3 + M$, which removes oxygen atoms and regenerates ozone, occurs less often since it requires a three-body collision. This is, of course, equivalent to an increase in the velocity of decomposition. The influence of nitrogen and helium, both of which increase the quantum yield compared with oxygen, is to be explained in the same manner as for the reaction in red light, *i.* e., nitrogen and especially helium are less adapted than oxygen in taking up the energy in a three-body collision.

The higher quantum efficiency in the ultraviolet may be explained in the following way. In the red we must expect that by the reaction $O_3 + h\nu \longrightarrow O_2 + O$ only a normal oxygen atom is formed, whereas in the ultraviolet the oxygen atom can contain much more energy, for the difference in energy between red ($\lambda \sim 620$ Å.) and ultraviolet ($\lambda \sim 2537$ Å.) is about 70 cal. Consequently, the reaction $O_3 + O \longrightarrow 2O_2$ which, as has been previously pointed out, occurs at every 2×10^3 collision, can now take place more frequently. From Warburg's experiments it can be calculated that the probability of the occurrence of this reaction is about 5×10^{-2}, assuming that the reaction $O + O_2 + O_2 \longrightarrow O_3 + O_2$ at a pressure of 1 atm. occurs at every 10^3 collision.

The reaction $O + O_3 \longrightarrow 2O_2^*$ is the only one that can initiate chains; therefore, the probability of chain formation is greater in the ultraviolet, where this reaction takes place more frequently than in the red. Another reason for the high velocity in the ultraviolet is to be found in the fact that the reaction of ozone with an excited oxygen atom can form oxygen molecules with 80 cal. excess energy, while in the reaction with a normal atom the excited oxygen molecule may have at the maximum 50 cal., since it is quite plausible to assume that the probability that ozone is excited by an oxygen molecule for reaction or decomposition is increased with increase in energy content of the latter. From the above considerations the higher quantum efficiency in the ultraviolet light is readily understandable. Warburg found at a total pressure of 1 atm., 90% O_2 and 10% O_3, the quantum yield **3.5.**

It is impossible to discuss the chains in detail since the behavior of concentrated ozone mixtures needs to be known and no experiments in this region are available.

The author has set up equations for $d[O_3]/dt$ for every possible reaction scheme considering the reactions between O_3, O, O_2 and O_2^*. Equations with more than four constants are always obtained and, as the value of some of these constants is not known, it is easy to represent the general course of the reaction by choosing suitable values for them. It is, however, impossible to find an equation which gives, for small concentrations of ozone ($\leqq$ 0.5%) and high oxygen pressures, a constant quantum yield and also describes the course of the reaction. Warburg found for ozone concentrations between 0.2 and 0.5% a constant quantum yield of 0.28; at higher concentrations, however, the velocity depends greatly on the ozone concentration and even for $O_3 \sim 0.75\%$ a quantum yield of 0.48 is obtained. This sudden transition to a zero order reaction is highly improbable. Furthermore, his results do not agree with those obtained by Regener and v. Bahr, who found a dependence of the velocity on the ozone concentration even in very dilute ozone mixtures. In the experiments of Warburg, as he himself states, there was always present an uncontrollable dark reaction which, with the long exposure necessary for a measurable amount of reaction to take place at low pressures, would be sufficiently large to obscure any expected small change in the quantum yield. It would, however, be very desirable to have these experiments repeated.

If the observation that water vapor accelerates the decomposition is correct, it can be accounted for by the reaction of excited oxygen atoms with water vapor.

In conclusion it may be said that the decomposition of ozone in the ultraviolet, as well as the influence of foreign gases and total pressure, can be explained if the primary reaction is assumed to be a dissociation into an excited oxygen atom and an oxygen molecule. It must, however, be emphasized that further experiments in this region would be of great use in order to elucidate the details of chain formation.

The author is greatly indebted to Dr. G. B. Kistiakowsky for permission to use his unpublished experiments. Thanks are also due Dr. O. R. Wulf of Washington, who kindly communicated the results of his investigations of the spectrum of ozone, and Dr. E. O. Wiig for translating the paper into English.

Summary

1. A critical survey of the experimental data involving the photochemical decomposition of ozone has been given.

2. The kinetics of the reaction have been explained on the assumption that the ozone spectrum shows predissociation and that the primary process is therefore $O_3 + h\nu \longrightarrow O_2 + O$. In red light a normal oxygen atom is assumed to be formed and in the ultraviolet an excited atom.

3. The probability of the occurrence of the reaction $O + O_3 \longrightarrow 2O_2$ has been calculated to be 5×10^{-4} if the oxygen atom is normal and it is assumed that the reaction $O + O_2 \longrightarrow O_3$ occurs only in a three-body collision.

4. The influence of temperature and of foreign gases has been discussed. The effect of gases which do not react with ozone can be interpreted by their specific influence on the three-body reaction $O + O_2 + M \longrightarrow O_3 + M$.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

PREPARATION AND PROPERTIES OF LEAD PERCHLORATE

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Introduction

Lead perchlorate was first prepared by Serullas[2] by heating lead oxide with perchloric acid. It was also prepared by Marignac[3] and Roscoe[4] by adding lead carbonate to perchloric acid and evaporating to a sirupy liquid. Roscoe was the first to point out the fact that lead perchlorate is extremely deliquescent. The formula of the salt which he obtained was $Pb(ClO_4)_2\cdot$-

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[1] From a dissertation submitted by J. L. Kassner to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Serullas, *Ann. chim. phys.*, *46*, 297 (1831).

[3] Marignac, "Oeuvres Complètes," Vol. I. p. 401 (1840–60); *Compt. rend.*, 42,288 (1856); *Mem. Soc. Phys. Genève,* 14,260 (1855); *Arch. Phys. Nat.*, *31*, 170 (1856).

[4] Roscoe, *Proc. Roy. Soc.* (London), 11, 493 (1861); *Ann.*, 121, 346 (1862); *J. Chem. Soc.*, 16, 82 (1863).

$3H_2O$. There is no record of any other hydrate of lead perchlorate, although Hoffmann[5] interpreted Roscoe's figures as corresponding to the formula, $Pb(ClO_4)_2{\cdot}1.5H_2O$.

Two forms of basic lead perchlorate have been described by Marignac,[3] Weinland[6] and Weinland and Stroh.[7] Marignac prepared the basic salts by boiling a concentrated solution of normal perchlorate with a slight excess of lead carbonate and evaporating the filtrate. The formula of his salt was $PbO.Pb(ClO_4)_2.2H_2O$. Rammelsberg[S] also prepared this same salt. Weinland[6,7] prepared basic lead perchlorates to which he ascribed the formulas, $Pb_2(ClO_4)_2(OH)_2{\cdot}1.5H_2O$ and $Pb_3(OH)_4(ClO_4)_2$. He prepared the first by treating lead oxide with more than one and less than two equivalents of perchloric acid. The latter was prepared by treating three moles of lead oxide with two moles of perchloric acid and crystallized in two forms as described by Marignac.[3]

Experimental

Preparation of Normal Lead Perchlorate.—Lead perchlorate was prepared by adding to lead nitrate about 1% excess over the calculated amount of perchloric acid and evaporating to remove all nitric acid. Lead nitrate of C. P. grade was twice recrystallized with centrifugal drainage and washing. Perchloric acid (72%) of a high degree of purity was further purified by fractional distillation in a vacuum. It was diluted with a little water, added to the lead nitrate and the solution evaporated until fumes of perchloric acid were given off. The lead nitrate did not entirely dissolve in the acid at first but gradually went into solution as the evaporation progressed. The solution was tested for nitrate from time to time by adding a drop of it to a solution of diphenylamine in concd. sulfuric acid, and the fuming was continued until no test for nitrate was obtained.

Removal of **Excess** Perchloric Acid.—Owing to the great solubility of the salt, it was found impossible to remove the excess of perchloric acid even by two recrystallizations. It could not be volatilized by heating because anhydrous lead perchlorate, stable up to 200°, begins to decompose above that temperature into lead chloride and lead oxide, evolving both oxygen and chlorine, and also because the last traces of acid, becoming anhydrous, readily decompose into chlorine and oxygen, contaminating the salt with chloride. Moreover, the salt containing excess of perchloric acid was decomposed slightly when dehydrated in a vacuum in the presence of phosphorus pentoxide.

The obvious method of neutralizing the excess of acid by the addition of lead oxide or carbonate is not readily applicable in this case, because these substances are readily soluble in a solution of lead perchlorate, forming soluble basic salts and there is no way of knowing when just the proper amount has been added except by making rather troublesome analyses of the solution.

Because perchloric acid dihydrate, unlike the anhydrous acid, is very stable, it seemed probable that the excess of acid could be removed by passing a stream of moist air over the fused salt, as was done by Richards and Willard——ith lithium perchlorate.

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[5] Hoffmann, "Lexicon der anorg. Verbindungen," **1915**, Vol. I, p. **699.**

[6] Weinland, *Z. angew. Chem.*, *34*, **354 (1921).**

[7] Weinland and Stroh, *Ber.*, **55, 2706** *(1922).*

[8] Rammelsberg, *Handb kryst. phys. Chem.*, *1*, **318 (1881).**

[9] Richards and Willard, THIS JOURNAL, 32, 4 **(1910).**

This was found to be satisfactory and because it is the most effective method for many perchlorates, it will be described in some detail.

A heater was constructed from a 20 X 30 cm. beaker which was wrapped with damp sheet asbestos and wound with seventy turns of chromel ribbon, 0.2 × 1.6 mm. The heating unit for the bottom of the beaker was made by coiling together chromel ribbon and a strip of asbestos 1 cm. wide to form a disk of suitable size which, while damp, was pressed against the bottom of the beaker. The two heating units could be connected either in series or in parallel. The beaker was insulated by asbestos wool, held in place by sheet asbestos, and the whole supported on a base of asbestos board. The beaker was covered with a quartz plate. Air purified by passing it through a solution of silver nitrate and a soda-lime tower was passed through water at about 100° by bubbling it through a three-necked Woulff bottle, electrically heated by a winding of No. 28 chromel wire, and supplied with water from a large stock bottle. The moist air passed through a delivery tube extending to within 5 cm. of the bottom of the large beaker.

The lead perchlorate solution, free from nitrate, was evaporated below 125° until it contained only a little more water than was required to form the trihydrate. This solution was then placed in the heater described above, on a support 10 cm. high, and steamed for three hours at about 160°. At the end of this time the salt was free from acid and a nephelometric test[10] showed that it contained only a few thousandths of one per cent. of chloride.

If more than 1% excess of acid is used in preparing lead perchlorate, longer steaming will be necessary. The vapor pressure of water in the air passing through the heater must be high enough to prevent complete dehydration of the salt; otherwise considerable chloride will be formed.

In order to determine accurately the amount of free acid, a sample of 3 to 4 g. of the salt was dissolved in about 7 cc. of water free from carbon dioxide. The lead was precipitated as sulfate by the addition of excess of neutral sodium sulfate, and removed by filtration. The acid in the filtrate was determined colorimetrically by using brom thymol blue as indicator and 0.001 N hydrochloric acid and sodium hydroxide as standard solutions.

Crystallization of Lead Perchlorate.—Lead perchlorate is extremely soluble in water and the trihydrate melts at 83–84°. In order to obtain a satisfactory yield of crystals the amount of water present must be carefully regulated. It was found best to start with a known weight of lead nitrate and for every 500 g. of lead perchlorate trihydrate, to allow 8 to 10 g. excess of water. A semi-fluid mass was then obtained on cooling to 0°. The crystals were drained centrifugally in platinum cups and a yield of 58% was obtained. The trace of chloride originally present could not be detected nephelometrically after crystallization. The yield decreased rapidly as the amount of water increased beyond that required to form the trihydrate. For example, in the above case, 555 g. of the salt was present, and if 26 g. of water instead of 10 g. was present, no crystals appeared on cooling to 0°.

Preparation of Anhydrous Lead Perchlorate.—Lead perchlorate trihydrate, dried at room temperature with phosphorus pentoxide in a vacuum for nine months, was not completely dehydrated. To increase the rate of dehydration by drying in a vacuum at a higher temperature the following apparatus was devised. A flanged pyrex cylinder[11] 60 cm. long by 12.5 cm. inside diameter and 0.5 cm. thick, was provided with covers to which were fused glass stopcocks. The flanges and covers were so carefully ground that, using only a trace of grease, the cylinder maintained a vacuum. This cylinder was placed in an electric oven 25 × 30 × 28 cm., made of "transite" asbestos board. The

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[10] Richards and Wells, *Am. Chem. J.*, 31, 235 (1904).

[11] Specially made by the Corning Glass Works.

oven was wired in two units, the sides and bottom with twenty turns of No. 28 chromel wire and the top with twenty-two turns. There was a mica window on top and another on one side. The advantage of this apparatus was that the central portion of the cylinder, containing the salt to be dehydrated, could be heated to the desired temperature, while the ends, containing the desiccant, phosphorus pentoxide, were relatively cool.

Because anhydrous lead perchlorate takes up moisture with such extraordinary rapidity, it was necessary to handle it only in very dry air. A large tight box was constructed of wood with a plate glass top and large enough to manipulate three ordinary desiccators. It was provided with a door, made air tight by means of a soft rubber gasket. There were two "manipulating arm-holes" in which long-sleeved rubber gloves were fastened air tight. A sulfuric acid manometer was provided for observing the pressure. Air, dried successively by calcium chloride and phosphorus pentoxide. was passed into the box for a few hours before and during use.

Lead perchlorate trihydrate was placed in an evaporating dish supported in the center of the cylindrical pyrex desiccator described above. Phosphorus pentoxide placed in the cool ends of the cylinder served to remove the moisture. The oven was adjusted to maintain a temperature of 65°. It was evacuated to a pressure of 35 mm. and the drying continued for nineteen hours. The salt was then removed and weighed on a platform balance in the manipulating box. When the hydrated salt had lost about one-third of its water of hydration, the temperature was raised to 100° for eight hours and then to 120° for fourteen hours. Analysis of the salt at this time showed 50.73% of lead compared with a theoretical value of 51.02% for the anhydrous salt. The heating was continued at 120° for twenty-four hours and at the end of this time the salt contained 51.02% lead.

Analysis of Anhydrous Lead Perchlorate.—While still hot, the salt was removed from the vacuum desiccator and placed in an ordinary desiccator containing phosphorus pentoxide. This was then placed in the manipulating box along with a similar desiccator containing two tared weighing bottles with carefully ground stoppers. After flushing out the box with dry air, a sample was transferred to the weighing bottle, and replaced in the desiccator. The stoppers were so well ground that there was no gain in weight during the process of weighing.

The amount of lead in the salt was determined by precipitating it as lead sulfate and weighing on a Gooch crucible. Duplicate analyses gave 51.016 and 51.020% of lead as compared to a theoretical value of 51.02%.

Anhydrous lead perchlorate is white and when exposed to air takes up moisture with amazing rapidity, forming the monohydrate and trihydrate. It is stable at 200° but begins to decompose at about 250° into lead chloride and lead oxide, evolving both oxygen and chlorine. It fuses at 270–275°, and above this completely decomposes.

Preparation of Lead Perchlorate Monohydrate.—Lead perchlorate trihydrate was partially dried at room temperature in a vacuum desiccator with phosphorus pentoxide. It then contained a little more water than corresponded to the monohydrate (6.77% instead of 4.25%, calculated from a determination of lead). The pentoxide was then replaced by a large excess of anhydrous lead perchlorate and the desiccator evacuated. The salt was allowed to remain in this desiccator for fifteen months and then analyzed for lead and perchlorate.

To obtain samples without exposure to atmospheric moisture, the manipulating box was used as before. Lead was determined as sulfate and the perchlorate by precipitation with "nitron" as described by Storm[12] and also by removing the lead electrolytically and then titrating the acid with standard alkali using methyl red as indicator. The results were as follows. Calcd.: Pb, 48.85%; ClO_4, 46.90%. Found: Pb, 48.85,

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[12] Storm, U. S. Bur. of Mines, Bull. 96, 1916, p. 65.

48.85; ClO_4, 47.06 (nitron), 46.67 (acid titration). A test of the methods of determining perchlorate showed that the nitron method, using twice the theoretical amount of reagent, was excellent and that no correction for solubility loss was necessary if the precipitate was transferred by means of the filtrate and washed with 10 cr. of ice water, added in 1–2 cc. portions, using slight suction. The removal of lead electrolytically tended to give slightly low results, perhaps due to slight loss by spraying. Precipitation of the lead by means of hydrogen sulfide and removal of the latter by boiling gave good results. No matter what method is used. the determination of perchlorate is less accurate than that of lead.

The melting point of $Pb(ClO_4)_2 \cdot H_2O$ was found to be 153–155". The above data prove the existence of this hydrate, which has not previously been obtained, and indicate that there is no lower hydrate.

Preparation of Lead Perchlorate **Trihydrate.**—A sample of lead perchlorate which had just been recrystallized was used. It contained 12.10% water as compared with 11.74% for the trihydrate. It was placed in a vacuum desiccator over a large excess of the monohydrate and the desiccator evacuated. It was allowed to stand for twelve months and then analyzed. Calcd.: Pb, 45.03; ClO_4, 43.73. Found: Pb, 45.17, 45.15; ClO_4 (nitron), 43.55, (acid titration), 43.20. The melting point of the trihydrate was 83–84°. The above data show the existence of the trihydrate and that another hydrate does not exist between the tri- and monohydrate.

Preparation of Basic Lead Perchlorate, $Pb_3(OH)_4(ClO_4)_2$.—This salt was prepared by saturating a hot solution of perchloric acid with lead oxide. The excess lead oxide was filtered out of the hot solution using a hot water funnel. On cooling, the basic salt crystallized in large irregular crystals. It was centrifuged in platinum cups and washed twice on the centrifuge with hot water. The salt was then crystallized from carbon dioxide-free water, centrifuged and washed. Weinland and Stroh[7] state that this salt may be prepared by treating three moles of lead oxide with two moles of perchloric acid. When attempting to prepare other basic lead salts than those described by Weinland, it was discovered that this same salt could also be prepared by using lead oxide and perchloric acid in the molecular ratio of four to three. When the ratio of lead oxide to perchloric acid was less than 4 to 3 and greater than 2 to 3, a mixture of the above basic salt and another, described later, was obtained This shows that the limits of the ratio for this basic salt are between 4 of oxide to 3 of acid and the saturation point of hot perchloric acid with lead oxide. The results of analysis are as follows. Calcd.: Pb, 69.96; ClO_4, 22.39; OH, 7.65. Found: Pb, 70.05, 70.00; ClO_4, 22.38, 23.36; OH, 7.65, 7.60.

The direct determination of hydroxyl was carried out as follows. The salt was dissolved in a slight excess of $N/10$ nitric acid. The solution was diluted and the lead precipitated as lead sulfate by adding excess of neutral sodium sulfate. After warming for a time it was cooled in ice and filtered. The excess acid was titrated with $N/10$ sodium hydroxide using phenolphthalein as indicator. It was observed that if the salt was dissolved in water, a turbidity appeared, probably due to a trace of carbonate, and if $N/10$ nitric acid was added slowly to the hot solution, the disappearance of the turbidity could almost be used as the end-point of the titration. It disappeared a trifle too soon, the difference being about 0.07 cc. of $N/10$ acid. Neither Marignac nor Weinland reported a determination of the hydroxyl group.

Preparation of $\mathbf{Pb_2(OH)_2(ClO_4)_2 \cdot 1.5H_2O}$.—Weinland and Stroh[7] state that this salt may be prepared from a solution of lead oxide in the calculated quantity of perchloric acid. An attempt was made to prepare this salt by his method, and also by varying the ratio of lead oxide to perchloric acid. Although the analysis indicated the existence of a salt of the above composition, it was not conclusive. The variation in the results seemed to indicate a mixture rather than a salt of definite composition.

The Solubility of Lead Perchlorate.—A slight excess of lead perchlorate trihydrate was added to water in a glass tube, which was sealed up and rotated for several days in a thermostat at 25 ±0.005°. After settling for several days, some of the clear liquid was transferred to a pycnometer with a carefully ground stopper consisting of a tube with a capillary bore. The capacity of the pycnometer at 25" was found to be 9.9783 g. of water, or 10.0180 cc. The weight of lead perchlorate solution required to fill it was 27.7950 g., or 27.8029 g. corrected to vacuum. The calculated density is 2.7753. The solution was transferred to a beaker, precipitated as lead sulfate, filtered and weighed on a Gooch crucible after heating at 600°. The corrected weight of $PbSO_4$ was 16.9111 g., equivalent to 22.6464 g. of $Pb(ClO_4)_2$ or 25.6603 g. of $Pb(ClO_4)_2 \cdot 3H_2O$. The following table shows the solubility calculated from these figures.

TABLE I

SOLUBILITY OF LEAD PERCHLORATE IN WATER AT 25°

Density, 25°/4°, 2.7753

	G per 100 cc. of soln.	G. per 100 g. of soln.	Mole per 100 cc. of soln.	Mole per 100 g. of soln.
$Pb(ClO_4)_2$	226.103	81.472	0.55676	0 20061
$Pb(ClO_4)_2 \cdot 3H_2O$	256.200	92.315		

Thiel and Stoll[13] called attention to the high density of the saturated solution and suggested its use as a heavy liquid for determining the specific gravity of organic substances. They stated that a solution saturated at 15° had a density of about 2.6 and contained 78% of lead perchlorate.

Anhydrous lead perchlorate is readily soluble in many organic solvents but work along this line was discontinued after the violent explosion of an almost saturated solution of this salt in anhydrous methyl alcohol. This solution was prepared by adding the perchlorate in small amounts to the alcohol, cooling after each addition because considerable heat was given off during this process. The solution was cooled in ice to see if crystals would form. This did not occur, and the solution was allowed to warm up to room temperature. A little more of the salt was added and when the flask was disturbed the contents exploded.

Summary

1. Anhydrous lead perchlorate, the mono- and trihydrates, have been prepared in a high degree of purity and their properties studied.
2. One basic lead perchlorate, $Pb_3(OH)_4(ClO_4)_2$, was prepared.
3. A method of determining the hydroxyl group in the basic salt is described.
4. The solubility of lead perchlorate in water at 25° is 81.472 g. per 100 g. of solution and the density is 2.7753.
5. A solution of anhydrous lead perchlorate in anhydrous methyl alcohol is explosive.

ANN ARBOR, MICHIGAN

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[13] Thiel and Stoll, Ber., 53, 2003 (1920).

[CONTRIBUTION PROM THE DEPARTMENT OF CHEMISTRY OP THE UNIVERSITY OF NORTH DAKOTA]

STUDIES IN AZO INDICATORS[1]

BY E. E. HARRIS, H. W. HAUGEN AND B. E. FAHL

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Since Sørensen's studies using indicators for the determination of hydrogen-ion concentrations, there has been a constantly widening use of indicators for the measurements in various fields. One of the difficulties has been that it required several different types of indicators having entirely different color changes to cover the PH range from 1.0 to 14.0. Each of these has individual characteristics which make knowledge gained from the use of one useless when it is necessary to use another. If a satisfactory series of indicators with the same color change could be prepared which would cover the whole PH range, their use would be greatly simplified. Certain groups are known to affect the color of dyes and should alter the color change of indicators. This paper is the report of a study made to determine the effect of substitution in the benzene nucleus and the position of this substitution on indicators of the methyl orange and methyl red type. Published work of this nature has been given in the paper of A. Thiel,[2] this deals with substitutions in naphthylamino-azobenzene. Several compounds which contribute to such a study are included in the work of Clark.[3]

Studies in Derivatives of Methyl Orange

Methyl orange has long been used as an indicator and several theories have been proposed for its color changes.4 The following work is to determine the effect of changing the position of the "diazo" group relative to the sulfonic acid group about the benzene ring on the ease of the electron shift, and also to determine the effect, if any, when substituent groups are introduced into either the benzene sulfonic acid part of the molecule or the dimethylaniline part, on this electron shift.

The method which was used for preparing the various diazo compounds was a modification of the one described in Gattermann.[5] The hydrogen-ion concentration at which color change took place was determined by a modification of the method of Fales and Mudge.[6]

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[1] This communication is an abstract of theses submitted by Harold W. Haugen and B. Elwood Pahl in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of North Dakota.

[2] A. Thiel, C. *A.*, 18, 3568 (1924); Z. *anorg. allgem. Chem.*, 136, 393–405 (1924).

[3] Value given in Clark, "The Determination of Hydrogen Ions," p. 78, 3.1–4.4.

[4] Ostwald, Z. *physik.* Chem., *9*, 579 (1892); Stieglitz, THIS JOURNAL, 25, 1112 (1903); Vorlander, ***Ber.***, 36, 1485 (1903); Hantzsch, *ibid.*, 41, 1187 (1908); 46, 1537 (1913); 48, 158 (1915); Thiel, C. *A.*, 18, 56 (1924); ***Ber.***, **56B**, 1667–1671 (1923).

[5] Gattermann, "Practical Methods of Organic Chemistry," The Macmillan Co., New York, 1925.

[6] Pales and Mudge, THIS JOURNAL, 42, 2447 (1920).

Experimental Part

OBSERVATIONS

Diazo compound	PH between which color change took place
Methylorange	2.8–4.1
p-Dimethylamino-azobenzene-*o*-sulfonic acid	2.8–4.1[8]
Ethyl orange	2.8–4.5[9]
p-Dimethylamino-azobenzene-2-sulfonic acid	3.5–4.47
p-Dimethylaminobenzene-azo-4-methyl-benzene-2-sulfonic acid..	2.8–4.4[7]
p-Dimethylaminobenzene-azo-4-methylbenzene-2-sulfonic acid	2.9–4.1
p-Dimethylaminobenzene-azo-4-nitrobenzene-2-sulfonic acid	2.5–4.0
p-Dimethylaminobenzene-azo-4-methylbenzene-3-sulfonic acid	2.8–4.1
p-Dimethylaminobenzene-azo-4-aminobenzene-3-sulfonic acid	2.2–2.5

Studies in Derivatives of Methyl Red

It appears that methyl red undergoes two color changes while changing colors. This has been accounted for in the color theories of Stieglitz, Thiel[4] and Hantzsch. There are several references[10] in the literature for the preparation of methyl red but the method given by Clark and Kirner[11] seemed the best to follow. In many of the derivatives several modifications were necessary.

The method used for determining the indicator constant was by colorimeter[12] for that concentration when half of the indicator had changed.

EXPERIMENTAL OBSERVATIONS

Indicator	Approximate indicator constant
Methyl red[13]	6.05×10^{-6}
2-Carboxybenzene-azo-dimethyltoluidine	6.19×10^{-6}
5-Nitro-2-carboxybenzene-azodimethylanilne	3.04×10^{-5}
4-Nitro-2-carboxybenzene-azodimethylaniline..	$3\ 07 \times 10^{-5}$
m-Carboxybenzene-azodimethylaniline..	2.32×10^{-3}
p-Carboxybenzene-azodimethylaniline	$4\ 5 \times 10^{-3}$
p-Dimethylamino-azobenzene-*p*-phenylacetic acid	1.07×10^{-3}
p-Dimethylamino-azobenzene-*p*-bromo-*p*-phenylacetic acid	$4\ 37 \times 10^{-4}$

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[7] The value of the mid-point as determined by a modification of the Gillespie colorimeter as described in Clark, Ref. 3, p. 69, was 3.31, C. S. Slater, Master's "Thesis," University of North Dakota (unpublished).

[8] This compound seems to have many advantages over methyl orange for clear-cut color changes as an indicator for the same range.

[9] Value 3.5–4.5, given in Clark, Ref. 3, p. 86.

[10] Rupp and Loose, *C. A.*, **3**, 523 (1909); Tizard, *C. A.*, 5, 1222 (1911); Rupp, *C. A.*, **10**, 2214 (1912).

[11] Clark and Kirner, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1922**, Vol. II.

[12] This colorimeter was for two-color indicators as designed by G. A. Abbott of North Dakota and constructed by Bausch and Lomb.

[13] This value agrees with that of Clark, *C. A.*, **11**, 1443 (1918); THIS JOURNAL, 46, 581 (1924), but is much higher than the value obtained in a different manner by Theil and Dassler, *C. A.*, 18, 56 (1924).

Conclusions

1. Substitution of methyl groups produces very little effect on the hydrogen-ion concentration at which the indicator changes color.

2. The position of the acid group produces the greatest change in indicator properties. When in the ortho position the change takes place at the higher PH, when in para lower and lowest in meta.

3. The introduction of strongly negative groups such as the nitro group causes a change at a lower *P*H.

GRAND FORKS, NORTH DAKOTA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE CHAIN CHARACTERISTICS OF THE ETHYLENE–OXYGEN REACTION

BY ROBERT SPENCE[1] AND HUGH S. TAYLOR

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It is now well known that many reactions once thought to be of the simple classical type actually occur by a chain mechanism. Generally speaking, the existence of these chains has been demonstrated in one or more of three ways, by measuring the quantum yield in photochemical experiments, by studying the unusual kinetics of gaseous reactions, or by introducing some active material or "trigger" to start the chains. In the case of hydrocarbon oxidations, the photochemical method is not very convenient experimentally. Before making a study of the kinetics of these reactions it was considered advisable to demonstrate their chain character in a direct manner by the last of the methods mentioned above. The use of ozone as a "trigger" in gaseous reactions was first developed by Semenoff and Rjabinin[2] in the combustion of sulfur. An attempt has been made to apply ozone as a "trigger" to the ethylene–oxygen system at temperatures where sufficient reaction takes place to be measurable but well below the ignition point. Under these conditions ozone has an extremely short life, so that the actual amount employed in starting chains may be very much smaller than the amounts actually introduced into the gas stream. We would therefore obtain only a lower limit of ozone efficiency and of chain length in this manner.

Ethylene and oxygen (from cylinders), at measured rates of flow, and dried over phosphorus pentoxide, were passed through *a* reaction vessel maintained at a definite temperature in a furnace, then through a weighed tube of phosphorus pentoxide for a given time, the increase in weight being noted. With everything else constant, the oxygen was then partially

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[1] Commonwealth Fund Fellow.

[2] Semenoff and Rjabinin, *Z. physik. Chem.*, **1B**, 193 (1928).

ozonized by passing through a Brody's ozonizer and the increase in weight of the absorption tube again noted. This increase was many times the former increase, as the appended Table I shows.

TABLE I

OXIDATION OF ETHYLENE IN PRESENCE AND ABSENCE OF OZONE

T, °C.	C_2H_4 O_2	Normal increase (*a*), g.	Using O_3 (*b*), g	Ratio b/a	Time, min
298	1:2.5	00020	0 1290	64 5	30
298	1:2	0020	0878	87 5	15
350	1:2	0030	.1350	45 0	15
358	1:2	.0032	0506	15 8	15
388	1:2	0152	Exploded	..	15

Assuming that all the ozone introduced into the gas stream reacted to give water, the increase in fifteen minutes due to ozone alone would be 0.12 g.; hence these experiments do not afford conclusive proof of the existence of a chain mechanism. The explosion is significant in view of the fact that ethylene and oxygen normally do not explode until temperatures over 500° are reached. With ozone present, the system becomes very sensitive to shocks around 400° and often exploded at the turning of a stopcock.

In another series of experiments the solid and liquid products of the reaction were frozen out by a carbon dioxide–ether trap and the remaining gases analyzed. The ozonizer was calibrated so that any desired concentration could be obtained by varying the current in the 4000-volt transformer. To prevent explosions, the apparatus was made of thick-walled barometer tubing (2-mm. bore) as far as possible and, in order to prevent decomposition of the ozone before it reached the furnace, the oxygen inlet tube was cooled by water circulating through a lead coil surrounding the inlet. The reaction chamber was also considerably smaller than in the first series of experiments, having a capacity of about 8 cc. instead of 150 cc. To prevent explosions due to sudden pressure variations at the moment when a gas sample was to be collected, the gas was first allowed to stream from the furnace into the air. With the stopcock leading to the analysis buret open, the exit to the air was slowly closed by tightening a clip on a small rubber tube attached to the air exit. When the dead space of the collecting system was thoroughly swept out, a sample was collected in the gas buret in a given time, the pressure being maintained as far as possible constant throughout the procedure. The products collected in the trap appeared to be mainly formaldehyde and small amounts of a white solid, possibly a polymer. Carbon dioxide was absorbed by alkali in the gas buret, ethylene removed by bromine water and all the remaining gas except a small residue could be absorbed by pyrogallol. In order to make the two measurements under as nearly the same conditions as possible, oxygen, for the sake of rapidity, was generally obtained by difference, a few check determinations being made at intervals. Results are given in Table II. The effect of increasing temperature causes an apparent shortening of the chains but this is no doubt due to the thermal decomposition of the ozone. All the values derived for the chain length are greater than unity and hence constitute direct evidence for the existence of reaction chains in hydrocarbon combustions; a small amount of ozone reacting is able to cause additional amounts of oxygen to take part in the reaction.

TABLE II

OXIDATION OF ETHYLENE IN PRESENCE AND ABSENCE OF OZONE

T, °C.	Time, sec.	Residual gas in given time interval Without O_3 O_2	 C_2H_4	 With O_3 O_2	 C_2H_4	O_2 used due to O_3, cc.	O_2 supplied as O_3, cc.	Ratio
260	30	41.5 cc.	27.5 cc.	37 cc.	25 cc.	4.5	0.630	7.1
274	30	36	29	32	26	4	.630	6.35
283	30	34	28	32	24.5	2	.630	3.2
323	15	52.5	13.6	49	12.5	3.5	.960	3.64
342	60	63	56	59	52.5	4	1.344	3.0
351	60	62	58	60	54	2	0.840	2.4
356	15	49	18	47.5	16	1.5	.936	1.6
401	15	48.5	16.5	47	15	1.5	.936	1.6
410	15	48.5	17	47.5	15.5	1.0	.924	1.1
430	30	57.5	12.5	54.5	11.0	3.0	.920	3.26
430	30	57.5	13.5	56.5	12.5	1.0	.920	1.1
430	60	104.5	25.5	101	22	3.5	1.84	1.9
438	15	48.5	14.5	46	13	2.5	0.906	2.75

Since this work was completed, a study of the oxidation of ethylene from the standpoint of reaction kinetics has been published by Thompson and Hinshelwood.[3] They conclude that "between 400 and 500° the oxidation is probably a chain reaction." They suggest that "the first stage in the reaction is the formation of an unstable peroxide; if this reacts with more oxygen the chain ends, but if it reacts with ethylene, unstable hydroxylated molecules are formed which continue the chain." They conclude "that from a consideration of the temperature coefficient and the influence of foreign gases on the rate of reaction that the chains are probably not of great length." The present experiments therefore constitute an important line of auxiliary evidence with respect to the chain characteristics of this hydrocarbon oxidation and supplement the data already supplied by Pease[4] with respect to the chain nature of the oxidation of the saturated hydrocarbons.

We desire to acknowledge our indebtedness to the Commonwealth Fund which provided one of us (R. S.) with the Fellowship with the aid of which this work became possible.

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[3] Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), 125A, 277 (1929).

[4] Pease, THIS JOURNAL, 51, 1839 (1929).

Summary

The use of ozone as an initiator of reaction between ethylene and oxygen at temperatures below the normal reaction temperature in absence of ozone has been studied.

The results are consistent with the hypothesis that the oxidation process is a chain reaction.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

SOLUBILITY OF LEAD SULPATE, CHROMATE AND MOLYBDATE IN NITRIC AND IN PERCHLORIC ACID

BY H. H. WILLARD AND J. L. KASSNER[1]

RECEIVED MARCH 24, 1930 PUBLISHED JUNE 6, 1930

It has been shown by Thiel and Stoll[2] that the difference in potential between lead electrodes in 0.05 molar solutions of lead perchlorate and nitrate is 0.016 volt. From this they calculated the ratio of the concentrations of Pb^{++} in the two solutions to be 1:0.28. In connection with other work the present authors had noticed that lead sulfate, chromate and molybdate were less soluble in perchloric acid than in nitric acid of the same concentration. In order to investigate this matter more thoroughly, with the possibility of utilizing the results in analytical separations, the solubilities of these salts were determined in perchloric and in nitric acids of different concentrations, both with and without the addition of a common ion.

Experimental

Preparation of Lead Sulfate.—Lead sulfate was prepared by adding simultaneously from two burets dilute solutions of sulfuric acid and lead perchlorate to 800 cc. of slightly acidified water, with vigorous stirring. This gave a fairly coarse precipitate. It was washed with water five times by decantation, centrifuged in platinum cups and washed four times on the centrifuge.

Preparation of Lead Chromate.—Lead chromate was prepared in the same manner as lead sulfate, using lead perchlorate and potassium dichromate. The lead chromate was washed with water eight times by decantation, four times on the centrifuge, dried in a vacuum over phosphorus pentoxide and analyzed by electrometric titration with ferrous sulfate. The average of two closely agreeing analyses gave 16.09% chromium, compared to a theoretical value of **16.08%.**

Preparation of Lead **Molybdate.**—Lead molybdate was prepared in a similar manner by adding lead perchlorate and ammonium molybdate to hot water acidified with perchloric acid. After boiling the solution for a few minutes, the precipitate was washed eight times by decantation with hot 2% ammonium nitrate solution, centrifuged, and

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[1] From a dissertation submitted by J. L. Kassner to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Thiel and Stoll, *Z. anorg. allgem. Chem.*, **139, 317 (1924).**

washed eight times on the centrifuge. Since it has been pointed out by Weiser[3] that lead molybdate occludes ammonium molybdate, the salt was further purified by stirring about 10 g. in a liter of normal perchloric acid for twenty-four hours After it had settled, a 500-cc sample of the clear solution was analyzed for lead and molybdenum and found to contain an excess of the latter, which must have been occluded as ammonium molybdate and subsequently extracted by the acid. The lead molybdate which had been stirred in perchloric acid was centrifuged and washed with hot 2% ammonium nitrate. After ignition it was analyzed, lead and molybdenum being separated by the sulfide method.[4]

Anal. Calcd.: PbO, 60.78. Pound: 80.72, 60.76, 60.69, average, 60.72. Calcd.: MoO_3, 39.22. Found: 39.18, 39.14, 39.11, average, 39.14.

The lead molybdate possessed a yellowish-white tinge. This was also observed by Weiser.[3]

Preparation of Nitric and Perchloric Acids.—c. P. perchloric and nitric acids were redistilled in a vacuum. The different concentrations were made up from these by means of a hydrometer, using for perchloric acid the table by van Emster[5] and for nitric acid the densities given by Lunge and Ray.[6] The hydrometers were calibrated to read directly to 0.0005 at 15.5° and it was possible to estimate to 0.0001. The accuracy of this method of making up the acid concentrations was checked by titrating with standard alkali. The maximum error was about 0.002 M for higher concentrations and much less than this for the very dilute solutions.

Solubility Determinations.—Lead sulfate, lead chromate and lead molybdate were each placed in liter flasks and rotated with known concentrations of nitric and perchloric acids, respectively, in a thermostat which was not observed to vary as much as 0.001'. The water used in the acid solutions was twice distilled, using a block tin condenser and a quartz receiver. The flasks were closed with well ground stoppers covered with sheet rubber to keep the water in the thermostat from contact with the ground-glass joint. They were rotated for fifteen hours, then supported in a vertical position for two hours and the salt allowed to settle. Although the supernatant liquid was clear, the solutions were filtered through a platinum sponge filtering crucible into which they were siphoned directly from the flasks, the first portion being discarded. In this way it was possible to obtain samples absolutely free from particles of salt. A 500-cc. sample was taken for the low solubilities, and a 250- or 100-cc. sample for some of the higher ones. The results shown are the average of closely agreeing duplicates.

Solubility of Lead Sulfate in Perchloric and Nitric Acids.—Saturation of the solutions was carried out in quartz flasks with ground stoppers. After rotating lead sulfate in the thermostat as described, a 500-cc. sample was measured out, 1 cc. of concentrated sulfuric acid added and the solution

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[3] Weiser, J. *Phys. Chem., 20,* 640 (1916).

[4] Treadwell–Hall, "Quantitative Analysis," 7th ed., Vol. II, John Wiley and Sons, Inc., New York, 1928, p. 266.

[5] Van Emster, *Z. anorg. Chem., 52,* 270 (1907).

[6] Lunge and Ray, *Z. angew. Chem., 4,* 165 (1891).

concentrated in a quartz evaporating dish to about 23 cc. It was then transferred to a tared crucible, evaporated to dryness by means of a ring burner, and ignited at low red heat. It was possible to reproduce the weight of the crucible to within 0.05 mg. when the tare was ignited and cooled in the same way as the sample before each weighing. If the tare was not ignited each time, the variation was 0.1 mg. or more.

Solubility of Lead Sulfate **Using** a Common **Ion.**—The procedure was essentially the same except that the solutions were made up carefully from standard solutions so that when they were mixed and diluted to the required amount, the normalities would be as indicated in the tables. All the samples in which sulfuric acid furnished the common ion were analyzed by direct evaporation as explained above, except in a few cases in which the solubility was so low that lead was determined colorimetrically as sulfide.[7]

As there were no interfering substances present, the procedure was much simplified. A 500-cc. sample of the clear supernatant liquid was evaporated on the hot-plate and fumed until all the sulfuric acid was removed. The residue of lead sulfate was dissolved in ammonium acetate solution and diluted until the concentration of lead ion was low enough to determine colorimetrically, as determined by a preliminary test. Of this diluted solution, 25, 50 or 100 cc. (depending on the amount of lead present) was made ammoniacal with 5 cc. excess of concentrated ammonia water and diluted to a definite volume, as 100 cc. Lead sulfide was precipitated by adding 4 or 5 drops of the sodium sulfide solution. A standard was prepared in the same way and its color compared with that of the unknown. A blank was run in each case on the unknown before adding sodium sulfide. It was possible to check results within 5%.

In the solubilities in which lead perchlorate and lead nitrate furnished the common ion, it was necessary to determine the sulfate ion. This was done by removing most of the lead electrolytically from the original solution, concentrating the sample to about 75 cc. and removing the remaining lead. The solution was partially neutralized with sodium carbonate, after which the sulfate was precipitated with barium chloride. The weight of lead sulfate was calculated from the weight of barium sulfate obtained. The results are shown in Tables I and II.

It is interesting to note that the solubility of lead sulfate in perchloric acid increases up to a 2.0 M solution of acid and then decreases again, while the solubility of lead sulfate in nitric acid continues to increase with increasing acid concentration. Lead sulfate is much less soluble in perchloric acid than in nitric acid of the same concentration.

Solubility of Lead Chromate.—Saturation of the solutions with lead chromate was carried out in glass flasks with ground stoppers. The

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[7] *Scott, "Standard Methods of Chemical Analysis," 4th ed., D. Van Nostrand Co., New York, 1925, p. 281.*

TABLE I

SOLUBILITY OF LEAD SULFATE IN PERCHLORIC ACID AT 25°

Composition of solvent	$PbSO_4$ dissolved in 100 cc. G.	Millimole
0 1 M $HClO_4$	0.0278	0 0917
0.1 M $HClO_4$ + 0.005 M H_2SO_4	.0070	0230
0 1 M $HClO_4$ + 0 02 M H_2SO_4	,0024	.0079
0 1 M $HClO_4$ + 0.05 M H_2SO_4	,0013	,0043
0 1 M $HClO_4$ + 0.10 M H_2SO_4	.0010[a]	0033
0 1 M $HClO_4$ + 0 25 M H_2SO_4	.0008[a]	0026
0 1 M $HClO_4$ + 0 50 M H_2SO_4	0003[a]	0010
0 1 M $HClO_4$ + 0 50 M $Pb(ClO_4)_2$	0002	0007
0 5 M $HClO_4$	0528	,1742
0 5 M $HClO_4$ + 0 005 M H_2SO_4	0206	.0679
0 5 M $HClO_4$ + 0 01 M H_2SO_4	0137	.0451
0 5 M $HClO_4$ + 0 02 M H_2SO_4	0067	.0220
0 5 M $HClO_4$ + 0 05 M H_2SO_4	0030	,0099
1 0 M $HClO_4$	0714	2301
1 0 M $HClO_4$ + 0 005 M H_2SO_4	0367	1211
2 0 M $HClO_4$	0787	2596
3 0 M $HClO_4$	0687	2266
4 2 M $HClO_4$	.0490	1616

[a] Lead determined colorimetrically

TABLE II

SOLUBILITY OF LEAD SULFATE IN NITRIC ACID AT 25°

Composition of solvent	$PbSO_4$ dissolved in 100 cc G.	Millimole
0 1 M HNO_3	0 0426	0.1405
0 1 M HNO_3 + 0 005 M H_2SO_4	.0078	.0257
0 1 M HNO_3 + 0.05 M H_2SO_4	0015	0049
0 1 M HNO_3 + 0 25 M H_2SO_4	0011	.0036
0 1 M HNO_3 + 0.50 M H_2SO_4	.0009	.0030
0 1 M HNO_3 + 0 50 M $Pb(NO_3)_2$	.0008	.0026
0 5 M HNO_3	0992	.3272
0 5 M HNO_3 + 0 005 M H_2SO_4	0398	,1313
0 5 M HNO_3 + 0 01 M H_2SO_4	0328	.1082
0 5 M HNO_3 + 0 02 M H_2SO_4	0159	0524
0 5 M HNO_3 + 0 05 M H_2SO_4	0089	,0293
1.0 M HNO_3	2021	.6667
1 0 M HNO_3 + 0 005 M H_2SO_4	.1007	.3322
2 0 M HNO_3	3605	1 1890
3.0 M HNO_3	.5389	1.7770
4 2 M HNO_3	,7263	2 3960

amount of lead chromate dissolved in the various concentrations of perchloric acid was determined by adding potassium iodide and titrating the iodine liberated with sodium thiosulfate using starch as indicator. For those in nitric acid the lead chromate was titrated electrometrically with 0.1 or 0.01 N ferrous sulfate. The solutions were concentrated to 150–200 cc., with addition of sulfuric acid when necessary, and cooled in ice before titrating. When lead perchlorate and lead nitrate furnished the common ion, the chromate was determined by electrometric titration with ferrous sulfate. When sodium dichromate was used, the solution was analyzed for lead by reducing the dichromate with hydroxylamine hydrochloride, adjusting the acidity of the solution, and precipitating the lead with hydrogen sulfide. The lead sulfide was filtered, washed and dissolved in dilute nitric acid. This solution was boiled, neutralized and diluted to a suitable definite volume. Lead was then determined colorimetrically as described above. The results are shown in Tables III and IV.

TABLE III

SOLUBILITY OF LEAD CHROMATE IN PERCHLORIC ACID AT 25°

Composition of solvent	$PbCrO_4$ dissolved in 100 cc. G.	 Millimole
0.1 M $HClO_4$	0.0041	0.0127
0.1 M $HClO_4$ + 0.005 M $Pb(ClO_4)_2$	.0000	.0000
0.5 M $HClO_4$	.0120	.0371
0.5 M $HClO_4$ + 0.005 M $Pb(ClO_4)_2$	.0005	.0015
0.5 M $HClO_4$ + 0.01 M $Pb(ClO_4)_2$	.0000	.0000
1.0 M $HClO_4$	.0140	.0433
1.0 M $HClO_4$ + 0.005 M $Pb(ClO_4)_2$	.0013	.0040
1.0 M $HClO_4$ + 0.01 M $Pb(ClO_4)_2$	.0000	.0000
2.0 M $HClO_4$	.0199	.0616
2.0 M $HClO_4$ + 0.01 M $Pb(ClO_4)_2$	.0012	.0037
2.0 M $HClO_4$ + 0.015 M $Pb(ClO_4)_2$	.0006	.0019
3.0 M $HClO_4$	.0211	.0668
4.0 M $HClO_4$	.0213	.0659
5.0 M $HClO_4$	.0191	.0591
5.0 M $HClO_4$ + 0.02 M $Pb(ClO_4)_2$	.0001	.0003
5.0 M $HClO_4$ + 0.03 M $Na_2Cr_2O_7$	.0000	.0000

TABLE IV

SOLUBILITY OF LEAD CHROMATE IN NITRIC ACID AT 25°

Composition of solvent	$PbCrO_4$ dissolved in 100 cc. G.	 Millimole
0.1 M HNO_3	0.0063	0.0195
0.1 M HNO_3 + 0.005 M $Pb(NO_3)_2$	.0001	.0003
0.1 M HNO_3 + 0.01 M $Pb(NO_3)_2$	.0000	.0000
0.5 M HNO_3	.0177	.0548
0.5 M HNO_3 + 0.005 M $Pb(NO_3)_2$	.0018	.0055
0.5 M HNO_3 + 0.01 M $Pb(NO_3)_2$	.0000	.0000
1.0 M HNO_3	.0385	.1190
1.0 M HNO_3 + 0.01 M $Pb(NO_3)_2$	.0038	.0117
2.0 M HNO_3	.0889	.2752
2.0 M HNO_3 + 0.15 M $Pb(NO_3)_2$	.0012	.0037
2.0 M HNO_3 + 0.25 M $Pb(NO_3)_2$	.0002	.0006
2.0 M HNO_3 + 0.30 M $Na_2Cr_2O_7$	.0002	.0006
3.0 M HNO_3	.1701	.5265
3.0 M HNO_3 + 0.02 M $Pb(NO_3)_2$	.0381	.1179
4.0 M HNO_3	.2812	.8700
5.0 M HNO_3	.4367	1.3510

In the case of lead chromate the solubility in perchloric acid increases up to 4.0 M acid and then begins to decrease, while the solubility in nitric acid continues to increase with increasing concentration of acid. Lead chromate is much less soluble in perchloric acid than in nitric acid of the same concentration.

Solubility of Lead Molybdate.—The solubility determinations of lead molybdate were carried out like those for lead chromate, and the supernatant liquid analyzed for both lead and molybdenum. This was done by adding 4–6 cc. of concentrated sulfuric acid and evaporating to remove the perchloric acid or nitric acid. The solution was diluted, the lead sulfate filtered off, washed with 0.5% sulfuric acid, ignited and weighed. If molybdenum is carried down it is detected by a bluish tinge around the edge of the precipitate during ignition. After adjusting the acidity of the filtrate, the molybdenum was reduced to a trivalent salt by passing it through a Jones reductor, received in a ferric alum and phosphoric acid solution and titrated with permanganate.[8] Perchloric acid must be absent because it oxidizes trivalent molybdenum even in dilute solution. The solubilities were discontinued at 1 *M* nitric and 3 *M* perchloric acid, because the molybdate seemed to be decomposed by the more concentrated acids, forming MoO_3.

Two methods were used for determining the solubilities of lead molybdate when lead perchlorate and lead nitrate furnished the common ion. First, when the concentration of the salt giving the common ion was not greater than 0.05 M, the procedure was the same as that above, except that the supernatant liquid was analyzed only for molybdenum. With lower solubilities, where greater accuracy was required, the colorimetric method of King[9] was used, with certain modifications. A 500-cc. sample was prepared by evaporating to fumes with a slight excess of sulfuric acid. The lead sulfate was filtered off and the molybdenum determined colorimetrically. Fifty cc. of the solution containing 2–3 cc. of concd. hydrochloric acid, about 2 cc. of concd. sulfuric acid and 1.5 g. of potassium thiocyanate was placed in a separatory funnel with the ether and cooled to 0°; 1 cc. of stannous chloride solution was added and the mixture shaken immediately. Two ether extractions were made, using 70 and 30 cc., respectively, but no color was obtained in the second.

When sodium molybdate furnished the common ion, the lead was separated by a double precipitation with alkaline sulfide,[4] converted into sulfate, dissolved in ammonium acetate to free it from silica, and determined colorimetrically.[7]

The results are shown in Tables V and VI.

Lead molybdate, like the sulfate and chromate, is much less soluble in

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[8] **Ref. 7, p. 319.**

[9] King, *Ind. Eng. Chem.*, **15**, **350** (1923)

TABLE V

SOLUBILITY OF LEAD MOLYBDATE IN PERCHLORIC ACID AT 25°

Composition of solvent	$PbMoO_4$ in 100 *cc.* G.	Millimole
0.10 M $HClO_4$	0 0016	0 0043
0.10 **M** $HClO_4$ + 0 01 **M** $Pb(ClO_4)_2$	0002	.0005
0 50 M $HClO_4$	,0136	0370
0.50 **M** $HClO_4$ + 0 01 **M** $Pb(ClO_4)_2$	0005	.0013
0 50 M $HClO_4$ + 0 02 M $Pb(ClO_4)_2$	0004	0011
0 50 M $HClO_4$ + 0 10 **M** $Pb(ClO_4)_2$	00006"	0001
0 50 **M** $HClO_4$ + 0.20 **M** $Pb(ClO_4)_2$	00004"	0001
0 50 **M** $HClO_4$ + 0 02 M Na_2MoO_4	.0004[b]	.0011
0 50 **M** $HClO_4$ + 0 05 **M** Na_2MoO_4	.00027[b]	0007
1.0 **M** $HClO_4$	.0373	.1016
2.0 M $HClO_4$	,1176	,3204
3 0 M $HClO_4$	2436	.6639

[a] **Mo determined colorimetrically.** [b] **Pb determined colorimetrically.**

TABLE VI

SOLUBILITY OF LEAD MOLYBDATE IN NITRIC ACID AT 25°

Composition of solvent	$PbMoO_4$ dissolved in 100 cc. G.	Millimole
0 10 **M** HNO_3	0.0020	0 0060
0 50 M HNO_3	,0244	.0665
0.50 M HNO_3 + 0 10 **M** $Pb(NO_3)_2$	.00032[a]	.0009
0.50 M HNO_3 + 0.20 **M** $Pb(NO_3)_2$	0002[a]	0005
0.50 **M** HNO_3 + 0.02 **M** Na_2MoO_4	.00064[b]	.0017
0.50 M HNO_3 + 0.50 **M** Na_2MoO_4	.0007[b]	.0019
1.0 M HNO_3	.1086	.2958

[a] **Mo determined colorimetrically.** [b] **Pb determined colorimetrically.**

perchloric acid than in nitric acid of the same concentration. The solubilities could not be carried far enough to determine whether it would pass through a maximum in perchloric acid as with lead sulfate and chromate.

The solubilities suggest a number of quantitative separations which are now being investigated.

Summary

1. The solubilities of lead sulfate, chromate and molybdate have been determined in perchloric and nitric acids, both with and without the addition of a common ion.

2. All these salts are much less soluble in perchloric acid than in nitric acid of the same concentration.

3. Both the sulfate and chromate pass through a maximum solubility in perchloric acid, and then, as the concentration of acid increases, the solubility decreases.

ANN ARBOR, MICHIGAN

[CONTRIBUTION PROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE VAPOR PRESSURE OF ALLENE AS A FUNCTION OF TEMPERATURE

BY ROBERT LIVINGSTON AND G. B. HEISIG

RECEIVED MARCH 28, 1930 PUBLISHED JUNE 6, 1930

Since there are at present no data on the vapor pressure of allene available in the literature, it seemed worth while to determine its vapor pressure at a series of temperatures, using a sample of the pure compound which was prepared by one of us (G. B. H.) in connection with a study of its radiochemical and photochemical properties.

The allene was prepared by the action of a suspension of zinc dust on 2,3-dibromo-propene-1. The latter substance was prepared according to the method of Lespieau and Bourguel.[1] The gas was condensed and sealed off in pyrex flasks. One of these flasks was later sealed to the all-glass apparatus and the gas was admitted to the apparatus by means of a magnetic breaking device. The allene was condensed in a liquid-air trap and distilled several times using liquid air as the condensing agent. Any permanent gases present were removed after each condensation by pumping off at a pressure of 10^{-5} mm. The higher-boiling substances were discarded in each distillation and the middle fraction of the final sample was used in this determination

The vapor pressures were measured with an open mercury manometer which was read with an accurate cathetometer. A correction of 1.4 mm. was made for capillary depression. The barometric pressure was recorded at half-hour intervals during the course of the work. The pressure measurements were reproducible within 0.2 mm. The tube containing the liquid allene was surrounded by a Dewar flask filled with an ether–alcohol mixture. The temperature of this bath was adjusted by adding solid carbon dioxide. The temperature measurements, which were reproducible within 0.1°, were made with an accurate platinum resistance thermometer, which was made and calibrated at the Cryogenic Laboratory of the U. S. Bureau of Mines. The calibrations were checked, at the time these measurements were made, at the ice point, 0.0°, and at the freezing point of carefully purified chloroform, −63.5°.

The observed values of the pressure and temperature are listed in the

TABLE I

VAPOR PRESSURE OF ALLENE AS A FUNCTION OF TEMPERATURE

T, °C.	−76 0	−65 4	−55 7	−45 4	−40 2	−36 5
P, mm. (obs.)	85 1	162 4	278 6	469 9	600 8	703 8
P, mm. (calcd)	85 1	162 5	279 3	469 9	599 6	709.6

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[1] Lespieau and Bourguel, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol V, p 49.

first two lines of Table I. Each of these values is the average of five or six independent measurements. It is improbable that the errors in the absolute values of the pressure and temperature are greater than 2 mm. and 0.2°, respectively.

The values of the pressure given in the last line were computed from the linear equation

$$\log P = -\frac{0.05223}{T} \times 20{,}852 + 7.455$$

The constants of this equation were obtained directly from the experimental measurements (not the averaged values) by the "method of averages." This equation yields, by a short extrapolation, a value at the normal boiling point of −35.0'.

Lespieau and Chavanne[2] measured the boiling points of both allene ($H_2C{=}C{=}CH_2$) and allylene ($CH_3C{\equiv}CH$). For allene they obtained a value of −32.0°, three degrees higher than the value presented here. Their work is not presented in sufficient detail to make a criticism of their experimental methods possible. It is noteworthy that their value for allylene (−23.5') is 4° higher than that based upon the very careful measurements of Maass and Wright.[3] It is not surprising that the vapor pressure equation obtained from the data of Maass and Wright for allylene

$$\log P = -\frac{0.05223}{T} \times 21{,}372 + 7.429$$

differs only slightly from that presented here for the closely related isomer, allene.

Summary

The vapor pressure of pure allene has been measured for the temperature range −76.1 to −36.5,° and these data have been fitted to a linear equation.

MINNEAPOLIS, MINNESOTA

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[2] Lespieau and Chavanne, *Compt. rend.*, 140, 1035 (1905).

[3] Maass and Wright, THIS JOURNAL, 43, 1098 (1921); "International Critical Tables," **1928,** Vol. III, p. 217.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

STUDY OF THE ADSORPTION OF WATER VAPOR AND CARBON DIOXIDE BY SAMPLES OF MANGANESE DIOXIDE AND HOPCALITE CATALYSTS

BY C. E. LANNING[1]

RECEIVED APRIL 12, 1930 PUBLISHED JUNE 6, 1930

Some time ago work in this Laboratory showed the great activity of manganese dioxide either alone or when mixed with other metallic oxides as an oxidizing catalyst.

These catalysts are capable of considerable variation as to composition but all possess a fineness of texture that renders them highly porous. Owing to their highly porous nature they tend to adsorb vapors readily and in the presence of gases having a considerable tension of water vapor, for instance, are likely to become "poisoned" by the condensation of liquid within the pores of the material. For this reason it was a matter of some interest to investigate the adsorption isotherms of these substances, especially with respect to water vapor and carbon dioxide.

Finely divided manganese dioxide has played a prominent role in the preparation of the most active catalysts of this type; also the conditions under which this oxide is prepared affect considerably its catalytic activity. Among the factors influencing the catalytic activity of the product is the alkalinity of the medium in which the oxide is prepared and consequently the amount adsorbed by the oxide. This effect of alkali might be to alter the degree of subdivision of the manganese dioxide or to alter the character of its surface. It was thought that the effect of alkali treatment on the structure of manganese dioxide could be determined by a careful study of the adsorption isotherms of the manganese dioxide after various treatments and in this way information gained that would be useful in preparing catalysts of this type. In addition it was hoped that such study would throw some light on the poisoning of the catalyst by water vapor, the possible poisoning by carbon dioxide, and the existence of definite hydrates of manganese dioxide which might have some influence on the activity of the catalyst.

Materials

The manganese dioxide was prepared according to the method of Frèmy,[2] which has been found to give uniformly a very finely divided product and to produce the most active catalyst. All samples were taken from this material. In each case the sample was screened and the granules between six and ten mesh selected for experimentation. These were kept in sealed bottles until used.

Sample 1.—The oxide was separated from adhering water as completely as possible

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[1] The above article forms part of the author's dissertation submitted in June, **1920,** for the Ph.D. degree and the work was carried out at the suggestion of J. C. W. Frazer.

[2] Fremy, *Compt.* rend., 82, **1231 (1876).**

on a Büchner funnel with a water pump. It was then placed in a press and subjected for forty-eight hours to a pressure of several tons per square inch. It was then removed and dried in an air-bath at 110° for three hours.

Sample 2.—The oxide was separated from liquid water on a Büchner funnel as above and dried for three hours in an air-bath at 140°.

Sample 3.—The oxide was dried on a Büchner funnel as above and for three hours in an air-bath at 140°. The material was then placed in a U-tube and for several days a current of a 1% mixture of carbon monoxide and nitrogen was passed over it at a temperature of 140°. Nitrogen was selected as a diluent to guard against overheating and prevent reoxidation.

Sample 4.—The oxide was dried as far as possible on a Büchner funnel. It was then suspended in a 0.1 N solution of sodium hydroxide, stirred thoroughly and allowed to stand for twenty-four hours. It was again dried as much as possible on a Buchner funnel and then for three hours in an air-bath at 140°.

Sample 5.—This sample was the catalyst, containing 63% MnO_2 and 37% Ag_2O.

Experimental

That these materials are very sensitive to changes in the moisture content of the air is shown by the following table giving results obtained by exposing two samples to the atmosphere alongside each other.

TABLE I

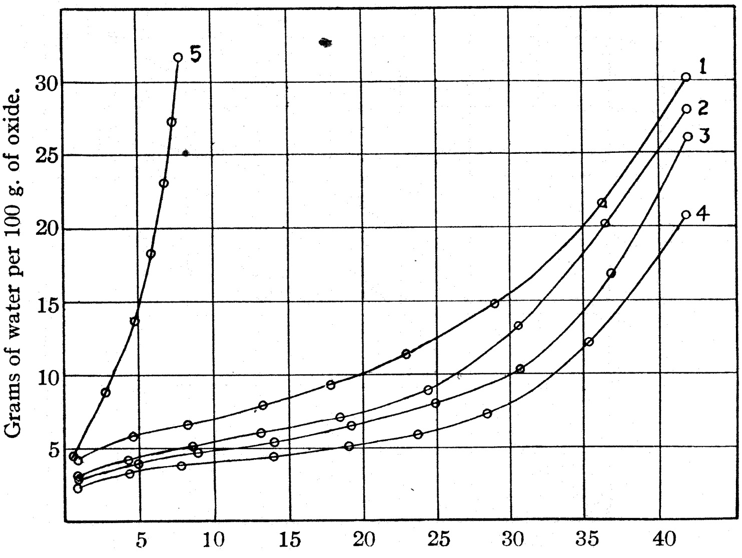
EXPERIMENTAL RESULTS

(1) a, 5.4762; b, 6.8397

Date	Sample a	Sample b	Pressure H_2O in air	% gain in wt. a	% gain in wt. b
7/26/1919	6.0068	7.4990	15.25 mm.	9.69	9.64
27	6.0391	7.5401	17.45	10.28	10.24
29	5.8193	7.2696	8.05	6.266	6.285
8/3/1919	5.8642	7.3271	9.5	7.086	7.127
7	6.0841	7.6092	19.35	11.101	11.250

Part I. Adsorption of Water Vapors

The apparatus used for the study of the adsorption of water vapor consisted of a series of ten glass bulbs containing sulfuric acid of different but known concentrations, to establish definite vapor pressures in the system. The concentration of acid used varied from pure water in Bulb 1 to concentrated sulfuric acid in Bulb 10. These bulbs were all sealed to the apparatus and each could be shut off from the remainder of the system by a mercury trap. The sample to be investigated was weighed into a small glass bulb which was provided with a ground-glass stopper and a side tube with a stopcock, which was attached to the system by means of a ground-glass joint. The whole apparatus was contained in an air-bath, the temperature of which was kept constant within 0.10 of a degree. Before beginning the measurements permanent gases were removed from all parts of the system, including the sulfuric acid contained in the bulbs mentioned above, and the small bulb containing the sample. The removal of the air dissolved in the bulb containing pure water, and those containing dilute sulfuric acid, was much more difficult than the removal from the bulb containing strong sulfuric acid; in fact, the permanent gases were given off quite readily from strong sulfuric acid, and the ease with which the dissolved gases could be removed appeared to vary, rather regularly, with the concentration of the acid. The removal of the permanent gases from the whole system is of very great importance, as it has been found that a small concentration of these permanent gases greatly delays the establishment of equilibrium. The manipulation of all parts of the apparatus was accomplished without the necessity of opening the bath. The vapor pressures in the system were determined by means of a cathetometer. The temperature of the bath during this investigation was 35°. The experimental results are shown below in Pig. 1, where, for comparison, there is included a graph of the values obtained by Anderson[3] at 18° for silica gel.



Pig. 1.—Adsorption of water vapor at 35°.

Part II. The Adsorption of Carbon Dioxide

The apparatus used for this part of the investigation was essentially that described by Patrick and McGavack.[4] The bulb containing the sample under investigation was kept at 0° by immersion in ice contained in a Dewar flask. The carbon dioxide used was obtained from a small cylinder of the gas, after allowing the permanent gases to escape as completely as possible. Here, again, permanent gases were removed completely from

[3] Anderson, *Z. physik.* Chem., 88, 191 (1914).

[4] Patrick and McGavack, THIS JOURNAL, 42, 946 (1920).

the whole system before the experiments were begun. The apparatus was carefully calibrated so that, from readings taken with the cathetometer, all of the data could be obtained for the accurate determination of the volume of carbon dioxide introduced into the system and the amount adsorbed at each stage by the sample. The results obtained are given in the form of curves in Pig. 2; again for comparison, the data on the adsorption of carbon dioxide by silica gel, as determined by Patrick,[5] were given. The only departure made in the regular routine procedure adopted was in the case of the sample which in its preparation had been exposed to a solution of caustic soda. In this case the sample was exposed for a considerable length of time to the action of carbon dioxide, which was subsequently pumped out of the apparatus before the experiment was begun.

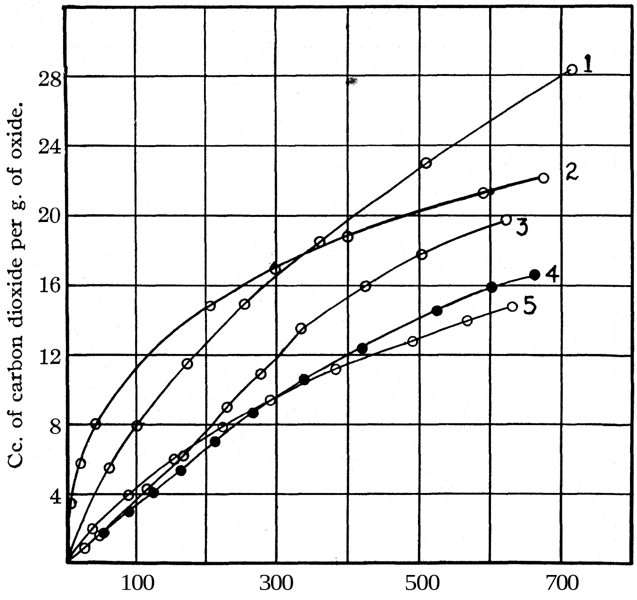


Fig. 2.—Adsorption of carbon dioxide at 0°.

Discussion

Since each point on the curves was duplicated, it is reasonably sure that they represent equilibrium conditions. This conclusion is made more definite because of the care taken in the complete removal of permanent gases from the system. Other work in this Laboratory has shown that in the presence of permanent gases it is very difficult to get true equilibrium in adsorption of vapors. These results show: (1) the highly porous, finely divided nature of all of these samples. Calculation of the approximate size

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[5] Patrick, "Inaugural Dissertation," Gottingen, 1914.

of the pores from the experimental data given above is not regarded as justifiable, but does indicate that the internal surface of these oxides is very high. (2) The adsorption curve of the sample prepared in the presence of caustic soda does not differ materially from the other curves, and the effect of alkali in depressing the catalytic activity of these oxides cannot be due to a change in the physical structure of the oxide. Other work in this Laboratory[6] has shown that when finely divided manganese dioxide is prepared in the absence of alkali it is extremely active catalytically. The effect of the alkali adsorption must, therefore, be that of a so-called "catalytic poison." **(3)** There is no evidence from any of these curves for the existence of definite hydrates.

Summary

The author has investigated the adsorption of water vapor and carbon dioxide on samples of finely divided manganese dioxide and mixtures of this oxide with other metallic oxides. The results are given in the form of curves and the shape of these curves shows that in neither case is there evidence of the formation of definite chemical compounds, but brings out clearly the very fine porosity of these substances.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

CYANOGEN IODIDE AS AN IMPURITY IN IODINE. ITS DETECTION AND ELIMINATION

BY SAMUEL MORRIS, E. B. CALLAGHAN, AND LUCILE DUNLAP

RECEIVED APRIL 14, 1930 PUBLISHED JUNE 6, 1930

Cyanogen iodide is commonly considered one of the chief impurities in commercial iodine. According to Dammer[1] iodine has been known to contain as high as 28.75% of this impurity. Baxter,[2] in his work on the atomic weight of iodine, took great care to eliminate cyanogen iodide. In the method which he used, iodine was suspended in water and treated with hydrogen sulfide, which formed hydriodic acid and, in case cyanogen iodide was present, hydrocyanic acid also. The separation of these two acids, as employed by Baxter, involved long-continued boiling and was based upon the separation of hydrochloric and hydrocyanic acids by the method of Richards and Singer.[3]

In the present paper, study was made first of the separation of known mixtures of hydriodic and hydrocyanic acids. This suggested a procedure for the detection of small quantities of –CN in iodine, which was worked out

[6] Whitesell, THIS JOURNAL, 45, 2841 (1923).

[1] Dammcr, "Handbuch der Anorg. Chem.," Vol. I, p. 542.

[2] Baxter, THIS JOURNAL, 26, 1579 (1904); 27, 876 (1905).

[3] Singer, Am. Chem. J., 27, 205 (1902).

upon samples of iodine with a known content of –CN, and then used for the detection of this impurity in samples of iodine on the market.

Materials

Iodine 1.—Mallinckrodt's C. P. iodine.

Iodine 2.—C. P. iodine which was further purified by reduction to hydriodic acid and subjection to long-continued boiling to remove any possible hydrocyanic acid.

Iodine 3.—Crude Chilean iodine obtained from Mallinckrodt Chemical Works.

Iodine 4.—Seaweed iodine obtained in 1920 from the U. S. Kelp Products Company, Summerland, California.

Iodine 5.—Baker's C. P. iodine.

Cyanogen Iodide.—The general method of preparation by Linnemann[4] was followed and a very pure product was obtained.

Experimental

By reducing mixtures of known weights of iodine and cyanogen iodide with hydrogen sulfide, mixtures of hydriodic and hydrocyanic acids of known concentrations were obtained. These mixtures were boiled in a balloon flask connected with an ordinary water-cooled condenser. The volume of the undistilled mixture was kept practically constant by adding water from time to time. Successive portions (10 to 12 cc.) of the distillate were collected and these tested for –CN by the ordinary qualitative test involving the formation of Prussian blue.

Preliminary experiments, the results of which are not recorded in this paper, showed that upon distilling dilute mixtures of hydriodic and hydrocyanic acids, the hydrocyanic acid was concentrated in the first portions of the distillate. After about two hours of boiling, the concentration of the hydrocyanic acid in the distillate was so low that 10-cc. portions failed to show any test for the acid.

In all experiments in Table I the above procedure was carried out, except that in Expts. 6 to 9 no ICN was added. In Expts. 1 to 5, Table I, the percentage of ICN added in succeeding experiments was steadily decreased.

TABLE I

EXPERIMENTAL DATA

Expt.	HI and HCN soln., cc.	Iodine sample	Iodine, g.	ICN added, g.	ICN, %	–CN, %	12-cc. portions of distillate Portion	–CN	Portion	–CN
1	500	1	8.994	0.029	0.323	0.055	1–4	Present	5–7	Absent
2	700	1	36.012	.031	.085	.014	1–5	Present	6–7	Absent
3	675	1	67.26	.0107	.015	.003	1–3	Present	4–7	Absent
4	700	1	133.93	.0109	.008	.0014	1–3	Present	4–7	Absent
5	1800	2	470.96	.0164	.00348	.0006	1–2	Present	3–7	Absent
6	700	1	57.31	...	....	..	1–6	Absent		
7	1700	1	455.0	...	....	..	1–7	Absent		
8	1700	3	412.0	...	....	..	1–23	Absent		
9	..	4	65.93	...	....	..	1–8	Absent		

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[4] Linnemann, *Ann.*, 120, 36 (1861).

The test for –CN in Expt. 5 was so slight, even in Portion I of the distillate, that the limit of detectability by this procedure, was considered substantially reached.

Since upon distilling mixtures of hydriodic and hydrocyanic acids the latter acid is concentrated in the first portion of the distillate, it seemed likely that by repeated redistillation the hydrocyanic acid could be concentrated in a small volume. To test this out, the first distillate was collected over a period of about nine hours and was large in volume. This in turn was distilled, but for a shorter time, resulting in a smaller distillate. After ten similar operations about 15 cc. remained, which was tested for –CN. This procedure was employed in all experiments in Table II, instead of the procedure involving a single distillation as used in Table I, and resulted in the detection of a considerably smaller percentage of –CN. The least amount detected by single distillation was 0.0006% in Expt. 5, while by repeated distillation, in Expt. 14, 0.00015% was detected.

TABLE II

RESULTS OF EXPERIMENTS

Expt.	HI and HCN soln , cc	Iodine, g	Iodine sample	ICN added, g	ICN, %	–CN, %	Times redistilled	–CN in final distillate
10	1500	226 0	5	None			10	None
11	1500	450 0	5	None			10	None
12	1500	450 0	2	0 0081	0 0018	0 000305	10	Present
13	1500	450 0	2	0016	00035	.00006	10	None
14	3000	902 0	2	0081	00089	00015	10	Present

In Expts. 6 to 11 samples of iodine from various sources on the market today were examined for –CN, but none was found. A larger sample of iodine of seaweed origin was desired for Expt. 9 but could not be obtained.

Summary

1. Hydriodic and hydrocyanic acids, in dilute solution, can be separated by boiling.
2. A procedure is given by which a small percentage of –CN in iodine (approximately 0.00015%) may be detected by the Prussian blue test.
3. No cyanogen iodide could be detected in samples of iodine on the market today.

MORGANTOWN, WEST VIRGINIA

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE REACTION BETWEEN NITROGEN AND HYDROGEN IN THE PRESENCE OF MERCURY VAPOR AND THE RESONANCE RADIATION OF MERCURY

BY W. ALBERT NOYES, JR.

RECEIVED APRIL 24, 1930 PUBLISHED JUNE 6, 1930

In a previous article[1] some experiments on the reaction between nitrogen and hydrogen in the presence of mercury vapor and the resonance radiation of mercury were described. It was pointed out that formation of ammonia was not observed either when a flow method was used or with low temperatures and low pressures of nitrogen, hydrogen and mercury vapor. Only at pressures of one atmosphere and higher and at the temperature of boiling mercury was there any observable formation of ammonia. In the article it was assumed that the important step was the formation of atomic hydrogen through the agency of excited mercury. A reconsideration[2] made it seem possible that the walls of the vessel may have exerted some influence on the reaction. Positive results, obtained under different conditions, have been reported by Hirst[3] and Willey and Rideal.[4]

Subsequently, Taylor and Marshall[5] have shown that monatomic hydrogen produced through the agency of excited mercury will not react with nitrogen to form ammonia under different experimental conditions. Bonhoeffer[6] has also shown that monatomic hydrogen produced by Wood's method[7] will not react with nitrogen to form ammonia.

All of these researches may be interpreted as showing that the production of monatomic hydrogen is not sufficient to initiate the reaction between hydrogen and nitrogen.[8] Recently, however, articles by Gaviola[9] and Beutler and Rabinowitsch[10] have given a possible explanation for the formation of ammonia under the conditions of the previous experiments.[1]

In Gaviola's experiments[9] the NH band at 3360–3370 Å. was observed in a mixture of N_2 and H_2 in the presence of excited mercury. The intensity of this band was proportional to the square of the intensity of the exciting light, a fact which led him to propose the primary mechanism $N_2 + 2Hg' = 2N + 2Hg$. The maximum energy available from two mercury atoms in

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[1] Noyes, THIS JOURNAL, **47**, 1003 (1925).

[2] Noyes and Kassel, *Chem. Reviews*, **3**, 199 (1926).

[3] Hirst, *Proc. Cambridge Phil. Soc.*, **23**, 162 (1926).

[4] Willey and Rideal, *J. Chem. Soc.*, 671 (1927).

[5] Taylor and Marshall, *J. Phys. Chem.*, **23**, 1140 (1925); Taylor, THIS JOURNAL, **48**, 2840 (1926).

[6] Bonhoeffer, *Z. physik. Chem.*, **119**, 385 (1926).

[7] Wood, *Proc. Roy. Soc.* (London), **102A**, 1 (1923).

[8] See B. Lewis, THIS JOURNAL, **50**, 27 (1928).

[9] Gaviola, *Nature*, **122**, 313 (1928); *Phys. Rev.*, **34**, 1373 (1929).

[10] Beutler and Rabinowitsch, *Z. physik. Chem.*, **6B**, 233 (1930).

the 2^3P_1 state corresponds to 9.8 volts, so that the heat of dissociation of nitrogen must represent a value lower than this amount. The heat of dissociation of nitrogen has been revised downward during the past few years and is now fixed at a probable value in the neighborhood of 9 volts.[11] Beutler and Rabinowitsch propose a mechanism involving two metastable mercury atoms (2^3P_0) each possessing an energy of 4.64 volts. This mechanism they give as follows: 2Hg (4.64 v.) = Hg (9.1 v.) + Hg + 0.18 v. and 2Hg (4.64 v.) + N_2 = N + N + 2Hg + 0.18 v. The production of monatomic nitrogen and the undoubted production of monatomic hydrogen should lead to the formation of some ammonia.[8] The first step may be N + H = NH (by triple collision or on the walls) or N + H_2 = NH + H, followed by NH + H_2 = NH2 + H and NH_2 + H_2 = NH_3 + H or by other processes involving triple collisions. It is not improbable that all of these reactions are possible energetically.

We may now inquire as to whether this mechanism agrees at all with the previously found facts.[12] The increase in total pressure would have the effect of broadening the absorption line of mercury, thereby increasing the amount of radiation absorbed and increasing the chance of reaction. Another effect would be the conversion of excited 2^3P_1 atoms into metastable 2^3P_0 atoms by collision. Since these have a longer life, the process described by Beutler and Rabinowitsch would become somewhat more probable. In addition the absorption would take place in a region nearer the walls, thereby effecting an increase in concentration of energy-rich atoms in a small region and increasing the probability of processes involving two of them.

It is to be noted that only small amounts of ammonia were formed, approximately the amount required at thermodynamic equilibrium. This is to be expected, since the excited mercury is known to cause the decomposition of this substance.'' Hence a steady state would be expected under a given set of conditions with the amount of ammonia at a low value.

Summary

Possible explanations for the previously reported formation of ammonia from nitrogen and hydrogen in the presence of mercury vapor and the resonance radiation of mercury have been discussed.

PROVIDENCE, RHODE ISLAND

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[11] See, for example, Birge, *Phys. Rev.*, **34**, 1062 (1929).

[12] A series of experiments was carried out subsequent to the publication of the previous article;' they gave results similar to those published.

[13] Dickinson and Mitchell, Proc. *Nat. Acad. Sci.*, **12,** 692 (1926); Taylor and Bates, *ibid.*, 12, 714 (1926); Bates and Taylor, THIS JOURNAL, **49,** 2450 **(1927).**

NOTES

A Note on the Density of **Glycine.**—A search of the literature and various handbooks reveals considerable confusion with reference to the density of glycine.

Landolt–Börnstein–Roth–Scheel give the density as 1.60. In the "International Critical Tables" the density is given as 1.160 at 20°. The value given by the "Handbook of Chemistry and Physics" is 1.161 at 15°. Beilstein gives the density of glycine as 1.161. Curtius[1] determined the density of glycine, obtaining the values of 1.1607.

The density of glycine was desired at 50°. The pycnometer method using xylene as the liquid being displaced was employed. Data were obtained with three different materials.

Eastman practical glycine gave an average value of 1.623 as the density at 50°, Eastman purified 1.5767, and Pfanstiehl purified 1.5740, the mean of the purified materials being 1.5753.

These results indicate a value of 1.5753 as the density, at 50°, of purified glycine. The results also seem to point to a typographical error in the original publication of Curtius, this value apparently being the source of the values given in the various handbooks.

COMMUNICATION NO. 428 RROM THE
KODAK RESEARCH LABORATORIES
ROCHESTER, NEW YORK

R. C. HOUCK

RECEIVED JANUARY 22, 1930
PUBLISHED JUNE 6, 1930

Differential Fractional Distillation.—Several authors[1] have shown that the original method of plotting potentiometric titration data (the electromotive force, E, against the volume of reagent, V) could be improved upon by plotting the slope of the above curve, $\Delta E/$ AV, as a function of V. The point of interest in the first type of curve is the point of inflection, while in the second type the point of interest is a sharp maximum. It seems that the common practice in plotting data from fractional distillation is to plot the volume of the distillate, V, against the temperature, T. In this curve, the boiling point of a component is a point of inflection. By direct analogy to the potentiometric titration, the author wishes to suggest that the fractional distillation data can be more readily interpreted if the slope of that curve, $\Delta V/$ AT, is plotted against T. In this derived curve the boiling point of each component would be a sharp maximum,

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[1] Curtius, J. prakt. Chem., 26, 158 (1882).

[1] Hostetter and Roberts, THIS JOURNAL, 41, 1341 (1919); Cox, *ibid.*, 47, 2138 (1925); MacInnes and Jones, *ibid.*, 48, 2831 (1926); Hall, Jensen and Baeckstrom, *ibid.*, *50,* 2217 (1928).

instead of a point of inflection, much more easily interpreted in the author's opinion.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
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P. M. GINNINGS

RECEIVED MARCH 12, 1930
PUBLISHED JUNE 6, 1930

Inorganic Lubricants. I. Amalgams.—The great specific gravity and the fluidity of mercury have long permitted its use as a floating and lubricating liquid in the support of astronomical and other heavy moving instruments. Bearings have been operated in a bath of mercury as lubricant.[1] It has been proposed also to use a film of mercury or amalgam as lubricant on metal bearings,[2] as well as "soft metals" such as copper–zinc amalgams.[3]

For some laboratory operations, such as those involving gases from which aqueous and organic vapors must be excluded, mercury or its fluid amalgams would be found useful as a lubricant for glass stopcocks and ground joints, except for the difficulty in obtaining an adherent film of the metal over the ground-glass surface and so securing the sealing of the joint. This difficulty may, however, be largely overcome in the following manner.

Carefully clean and dry the ground surfaces and then heavily silver them with ammoniacal silver nitrate and rochelle salt solution. Surfaces not to be silvered and passage openings may be protected by a thin layer of paraffin or ceresin wax. Immersion in as many as three to five fresh silvering solutions is usually necessary in order to secure the thickness of silvering required, although this depends upon the exact silvering formula used; too thick deposits obviously lessen the tightness of fit. After each deposition of metal the surface should be well rinsed in distilled water, but otherwise not disturbed.

The silvered surfaces finally obtained are then allowed to dry. Wax coatings on the passage openings should be entirely removed at this time. Amalgam paste or liquid is then dropped on the concave ground surface and the grinding parts are brought together and rotated gently with little contact pressure. Amalgamation of the silver rapidly takes place, and is complete when the motion is smooth and non-gritty, yielding a coherent film over the parts in contact, and tight lubrication.

These amalgamated surfaces are, as a rule, not permanent, but with care will endure through a number of operations lasting over several days, particularly if more amalgam is occasionally applied. They are rapidly destroyed on contact with aqueous solutions of many salts or with acid gases, and may not be used successfully with such materials, although when pure

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[1] Harper, U. S. Patent 994,920 (June 13, 1911).

[2] Sherwood, U. S. Patent 1,544,488 (June 30, 1925); 1,598,321 (Aug. 31, 1926).

[3] DeLattre and Hardy, U. S. Patent 1,559,077 (Oct. 27, 1925).

mercury is employed instead of an amalgam, an acid-resisting film is formed the ordinary life of which, however, is shorter than that of films formed with complex liquid amalgams.

The complex amalgam employed may be almost any dilute mercury solution. One such is a mixture of 5 g. of solder, 5 g. of Wood's metal, 2.5 g. of zinc and 80 g. of mercury, solution being effected with heat. Such a liquid also has the curious property of wetting clean, polished glass surfaces with ease.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
HARVARD COLLEGE
CAMBRIDGE, MASSACHUSETTS

WILLIS A. BOUGHTON

RECEIVED APRIL 12, 1930
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[CONTRIBUTION FROM THE UNIVERSITY OF OTAGO]

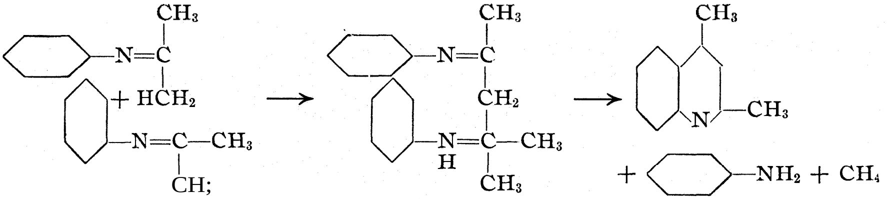
STUDIES IN QUINOLINE SYNTHESES

BY WILLIAM LYALL BARR

RECEIVED JULY 25, 1929 PUBLISHED JUNE 6, 1930

Historical.—The Skraup synthesis is variously formulated as involving intermediate formation of (I) acrolein anil, (II) β-anilinopropionaldehyde or (III) the anil of this aldehyde. The literature affords no definite evidence for the formation of a type I intermediate; there are results compatible with the formation of an intermediate of either type II or type III, but not of type I. Thus Murmann[1] obtained 2-phenylquinoline, not 4-phenylquinoline, by the condensation and oxidation of cinnamaldehyde and aniline, and Blaise and Maire[2] formed 4-ethylquinoline from anilinoethyl ethyl ketone heated with aniline hydrochloride.

From the work of Beyer, Engler and Riehm, and Knoevenagel, the last named investigator has shown[3] that quinoline formation from simple ketones or aldehydes and aromatic amines proceeds by the intermediate formation of ketylidene or alkylidene anils, which form dimerides and then quinoline derivatives; *e.* g., from aniline and acetone



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[1] Murmann, *Monatsh.*, 25, 621 (1904).

[2] Blaise and Maire, *Bull. soc.* **chim.,** [4] **3,** 658, 667 (1908).

[3] Beyer, *J. prakt. Chem.*, [2] 31, 47 (1885); 32, 125 (1885); 33, 393 (1886); *Ber.*, 20, 1767 (1887); Engler and Riehm, *ibid.*, 18, 2245 (1885); Knoevenagel and v. Baehr, *ibid.*, 55, 1912 (1922); Knoevenagel and Goos, *ibid.*, 55, 1929 (1922); Knoevenagel, Wagner and v. Baehr, *ibid.*, 56, 2414 (1923).

Any mesityl oxide or similar condensation product of the aldehyde or ketone is broken down to give the simple anil. The dimerides here mentioned are akin to the type III intermediate.

Another piece of evidence for the formation of the type III intermediate is the production of quinoline by Konig and Seifert[4] from $C_6H_5NHCH{=}CHCH{=}NC_6H_5$ heated with zinc chloride.

Theoretical.—Formation of a type I compound would involve reaction at only one double bond of a conjugate system, which is improbable, especially at a high temperature. Condensation of aniline with acrolein may be expected to be by the usual 1,4-addition. Polarity effects would lead to $C_6H_5NHCH_2CH{=}CHOH$, which can rearrange to the type II compound; but at the high temperature of the reaction, in the presence of aniline and the dehydrating agent, sulfuric acid, it is exceedingly unlikely that the aldehyde group would remain unattacked during the comparatively slow process of ring formation. Furthermore, as will be shown later, β-anilinopropionaldehyde polymerizes spontaneously to a substance from which no quinoline can be obtained.

Interaction of this aldehyde with aniline, however, would yield the type III compound, able to form quinoline by oxidation and splitting off of aniline, as shown by the work of Knoevenagel and of Konig and Seifert.

Experimental

In this work quinoline was detected in neutral aqueous emulsion or solution by the production with potassiomercurie iodide solution of a white amorphous precipitate which became yellow and crystalline on addition of dilute hydrochloric acid.[5] Recrystallized from hot water, this precipitate from quinoline melted at 144–146°.

The product of the direct interaction of acrolein and aniline, described by Mann,[6] was first studied; the observations that this base yielded no quinoline on treatment with sulfuric acid and arsenic oxide or nitrobenzene (Mann) or chromic acid (Konig) were confirmed. A similar negative result was found on oxidation with acid permanganate or ferric chloride. This base, $C_{18}H_{20}ON_2$, is evidently far more complex than the Skraup intermediate.

An attempt was made to carry out the series of reactions

$$C_6H_5NH_2 + ClCH_2CH_2CH(OEt)_2 \longrightarrow C_6H_5NHCH_2CH_2CHO \longrightarrow C_6H_5NHCH_2CH_2CH{=}NC_6H_5$$

Raeth's work[7] on this type of condensation of chloro-acetals with aromatic amines is spoiled by inconsistent nomenclature; and Konig and

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[4] Kbnig and Seifert, ***Ber.***, 56, 1853 (1923).

[5] Donath, ibid., 14, 1769 (1881).

[6] Mann, *J.* ***Chem.*** *Soc.*, 121, 2178 (1922).

[7] Raeth, ***Ber.***, 57, 550, 715 (1924).

Buchheim[8] have shown that in some of his work Raeth failed to identify the product correctly, and that no cyclization had occurred.

Direct interaction in dry ethereal solution of 1 mole of aniline and 1 mole of β-chloropropionacetal yielded aniline hydrochloride and, presumably, acrolein acetal. Use of excess aniline (2.5 moles) yielded aniline hydrochloride and a brown viscous liquid which, after removal of most of the aniline by distillation in *vacuo,* changed to a dark red solid gum, soluble in alcohol and acetone, which would not crystallize or distil without decomposition even *in vacuo.* The last traces of aniline could not be removed; yield, 20–25%; N, 7.0% (anilinopropionacetal, N, 6.3%). This crude residue yielded a tiny amount of quinoline on treatment with sulfuric acid and arsenic oxide or nitrobenzene. As free aniline was present, no conclusion can be drawn as to the-mechanism of the reaction.

Acid hydrolysis of this substance yielded, instead of β-anilinopropionaldehyde, a pink sticky gum which gave no aldehyde tests. An apparent polymer of this aldehyde was obtained by interaction of the chloro-acetal and a large excess of aniline in ether shaken with a saturated solution of sodium bicarbonate; distillation of the mixed bases in steam removed aniline and effected hydrolysis, leaving a brown resin soluble only in acetone and nitrobenzene; N, 9.4%; mol. wt. in nitrobenzene, 495 (anilinopropionaldehyde, N, 9.4%; mol. wt., 149). This aniline-free substance yielded no quinoline.

All attempts to condense the crude anilinopropionacetal base with aniline by the action of concd. hydrochloric acid or 70% sulfuric acid proved unsuccessful. Hence the type III intermediate was not obtained, and no conclusion can be drawn as to its place in the Skraup synthesis.

Attempts were made to effect cyclization with propionanilide and with allylaniline.

Propionanilide could not be made to undergo ring formation by heating with zinc dust, or with nitrobenzene and zinc chloride or sulfuric acid; nor by passing through a hot tube in air alone or over lead oxide.

Koenigs obtained quinoline from allylaniline vapor passed over lead oxide in a hot tube. Cyclization to quinoline was attempted under the conditions of the Skraup reaction.

Ten g. of allylaniline and 20 g. of sulfuric acid with 8 g. of nitrobenzene or 20 g. of arsenic oxide dried at 170° were refluxed for several hours, and the dark viscous mixture worked up for quinoline. There was much charring and production of tarry matter. Quinoline was detected in small quantities in every case; yield, about 1%. Picric acid was tried in place of nitrobenzene (*vide* Murmann), but it made the reaction explosively violent.

Based on a preparation of acrolein by Wohl and Mylo[10] from glycerol vapor passed over heated magnesium sulfate, a synthesis of quinoline was attempted from the vapors of aniline and glycerol aspirated in air or carbon dioxide over magnesium sulfate at 370–400°, with nitrobenzene vapor or lead oxide as oxidizing agent. No quinoline could be detected in the products of the reaction.

To try to reduce the number of distillations in steam in the Skraup synthesis from three to two, transformation of excess aniline to phenol with nitrous acid was tried in the

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[8] König and Buchheim, *Ber.,* 58,2868 (1925)

[9] Koenigs, *ibid.,* 12, 453 (1879).

[10] Wohl and Mylo, *ibid.,* 45, 2046 (1912).

acid reaction mixture after distillation in steam to remove nitrobenzene and dilution with water. These attempts were unsuccessful, for though excess nitrous acid was shown to be present, the resulting quinoline contained a considerable amount of aniline. The destruction of aniline was incomplete even with the clear reaction mixture obtained by the method of Cohn and Gustavson.[11]

The author wishes to express his grateful thanks to Dr. J. K. H. Inglis for his kind interest and helpful advice in this investigation.

Summary

1. As neither β-anilinopropionaldehyde nor its acetal or anil could be obtained pure, nothing can be concluded as to the constitution of the Skraup intermediate.
2. Allylaniline can yield small quantities of quinoline by oxidation in solution.

DUNEDIN, NEW ZEALAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

NITRIDATION STUDIES. I. INTRODUCTION. II. MERCURIC NITRIDE AND BISMUTH NITRIDE AS NITRIDIZING AGENTS[1]

BY IMAN SCHURMAN AND W. CONARD FERNELIUS

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I. INTRODUCTION

The term "nitridation" or "nitridation reaction"[2] has been applied to all those reactions which for the ammonia system of compounds are essentially similar to oxidation reactions for the familiar water compounds or for those reactions in which nitrogen plays a part analogous to that played by oxygen in ordinary simple processes of oxidation.

Numerous examples of nitridation reactions are known.[3]

The only agents to be examined to any extent, however, are hydrazoic

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[11] Cohn and Gustavson, THIS JOURNAL, 50, 2709 (1928).

[1] The material presented in this paper is from a portion of a thesis submitted by Iman Schurman in partial fulfilment of the requirements for the Degree of Master of Science at The Ohio State University.

[2] (a) Browne and Welsh, THIS JOURNAL, 33, 1728 (1911); Franklin, *J. Phys. Chem.*, *27*, 169 (1923); cf. Goldberg, THIS JOURNAL, 34, 886 (1912). Turrentine [*ibid.*, 34, 386 (1912)] calls hydrazoic acid a nitridizing agent because many of the reactions of hydrazoic acid are similar to those of nitric acid, an oxidizing agent. (b) Cady and Taft [*Science*, 62, 403 (1925)] have proposed the terms "electronation" and "delectronation" to be used in place of "reduction" and "oxidation" in the broad sense. Accordingly "nitridation" would be a particular type of "delectronation."

[3] Franklin, *J. Phys. Chem*, 27, 169 (1923); THIS JOURNAL, 46, 2142 (1924); "Reactions in Liquid Ammonia," Columbia University Press, New York, 1927, p. 16, Bergstrom, THIS JOURNAL, 48, 2324 (1926); *J Phys. Chem.*, 32, *440* (1928); Strain, THIS JOURNAL, 49, 1558 (1927); 50, 2220 (1928); 51, 271 (1929); Chuck, "Dissertation," Stanford University, 1925; Turrentine, Ref. 2a; Goldberg, Ref. 2a.

acid (ammono nitric acid) and a solution of iodine in liquid ammonia which undoubtedly contains iodo-amine, H_2NI, ammono hypoiodous acid.[4] In addition, certain electrolytic nitridations have been carried out.[5]

The present investigation was undertaken in an endeavor to increase our knowledge concerning nitridation and particularly to discover new nitridizing agents.

II. MERCURIC NITRIDE AND BISMUTH NITRIDE AS NITRIDIZING AGENTS

Mercuric oxide is a substance sometimes used as a mild oxidizing agent.[6] Its ammonia analog, mercuric nitride, should then be a mild nitridizing agent. The explosiveness of mercuric nitride[7] when dry is in harmony with this view. Hydrazobenzene was chosen as a substance to be nitridized because it has been oxidized to azobenzene by means of mercuric oxide[8] and nitridized electrolytically in liquid ammonia solution.[2b]

A preliminary nitridation using a solution of iodine in liquid ammonia showed that hydrazobenzene is easily converted into azobenzene. Mercuric nitride reacts with hydrazobenzene in accordance with the equation

$$3C_6H_5NHHNC_6H_5 + Hg_3N_2 \longrightarrow 3Hg + 3C_6H_5N{=\!=}NC_6H_5 + 2NH_3$$

p-Hydrazotoluene is likewise nitridized to *p*-azotoluene by both iodine and mercuric nitride.

Another nitride showing a considerable degree of instability is bismuth nitride.[9] In preparing this substance Franklin found that it is always contaminated with metallic bismuth as a result of its spontaneous decomposition. In harmony with this behavior of bismuth nitride, the present investigation shows that both hydrazobenzene and *p*-hydrazotoluene are nitridized to the corresponding azo compounds in liquid ammonia solution by bismuth nitride.

Whenever an hydrazo compound was added to either of the nitride precipitates, the solution above the insoluble nitride became dark red. Such behavior undoubtedly indicates either that mercuric and bismuth nitrides—although very insoluble in liquid ammonia—are, nevertheless, sufficiently soluble to give a weakly basic solution, or that the potassium amide had not been entirely removed from these nitride precipitates although the

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[4] For the reaction between iodine and ammonia see Mellor, "A Comprehensive Treatise," etc., Longmans, Greene and Co., New York, **1928**, Vol. VIII, p. 605–611; *cf.* also Bcrgstrom, *J. Phys. Chem*, *30,* 12 (1926).

[5] Browne, Holmes and King, THIS JOURNAL, **41,** 1769 (1919); Cady and Taft, *J. Phys. Chem.,* **29,** 1070 (1925).

[6] Gautier, *Ann. chim. phys.*, [4] **17,** 228 (1869).

[7] Franklin, THIS JOURNAL, **27,** 820 (1905); *Z anorg. Chem* , *46,* 1 (1905).

[8] Perkin and Kipping, "Organic Chemistry," J. B. Lippincott Co , Philadelphia, **1922,** p. 425. This reference seems to be the only one in the literature on the reaction of hydrazobenzene and mercuric oxide. Cf the similar preparation of phenyl azomethane from the corresponding hydrazine [Fischer, *Ber.*, **29,** 794 (1896)].

[9] Franklin, Ref. 7, p 847.

number of washings should have been sufficient to remove it. White and Knight[10] observed a similar coloration when a solution of hydrazobenzene or azobenzene was treated with a sodium solution and attributed their results to the formation of a salt, $C_6H_5N(Na)\text{-}N(Na)C_6H_5$. When a solution of hydrazobenzene or *p*-hydrazotoluene is treated with a solution of potassium amide, a brown coloration develops. Cady and Taft observed a similar coloration with sodium amide and hydrazobenzene. The present investigation has shown that this reaction with the alkali metal amides is a reversible one so that the hydrazo compounds, like triphenylmethane,[11] serve as very sensitive indicators of the Ostwald type in liquid ammonia. In pure liquid ammonia or in the presence of an ammonium salt (an acid) the hydrazo compounds yield a light brownish-yellow solution, while in the presence of soluble bases, even at very low concentrations, the deep red-brown color of the alkali metal salt appears. Even potassium hydroxide, whose solubility in ammonia is exceedingly low, imparts a distinct brown color to the solution of hydrazobenzene. Sodium peroxide is also sufficiently soluble in liquid ammonia to give a similar coloration.[2b]

Hexamethylenetetramine, amylene, styrene and azoxybenzene in liquid ammonia show no reaction with mercuric nitride over the space of one week.

Experimental

In carrying out the reactions described in this paper the familiar methods used by Franklin and his co-workers[12] have been employed. In one leg of a two-legged reaction tube was placed a convenient amount of purified and dried mercuric iodide or bismuth iodide; in the other, an excess of potassium, contained in a short length of glass tubing, together with a spiral of iron wire. On distilling ammonia into the reaction tube both the iodide and the potassium dissolved. In the presence of the iron wire catalyst the potassium was rapidly converted, usually in a half hour, into the soluble potassium amide.

After partially opening the stopcock for a moment to release the pressure of the evolved hydrogen, the solution of potassium amide was poured into the leg containing the iodide—an excess of potassium amide was necessary to prevent the formation of ammono-basic salts. The nitride precipitated and settled rapidly.

$$3HgI_2 + 6KNH_2 \longrightarrow Hg_3N_2 + 4NH_3 + 6KI$$
$$BiI_3 + 3KNH_2 \longrightarrow BiN + 2NH_3 + 3KI$$

These precipitates were washed by decantation with fresh ammonia about

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[10] White and Knight, THIS JOURNAL, 45, 1782 (1923).

[11] Kraus and Rosen, *ibid.*, **47**, 2743 (1925).

[12] Franklin, *ibid.*, **27**, 831 (1905); **29**, 1275 (1907); **35**, 1460 (1913); J. *Phys. Chem.*, *15*, 510 (1911); 16, 694 (1912); Fitzgerald, THIS JOURNAL, **29**, 1694 (1907); Bohart, J. *Phys. Chem.*, *19*, 539 (1915).

five times, to free them of potassium iodide and potassium amide. The solvent was next distilled into the leg containing the precipitated nitride. This leg was then cooled in a bath of liquid ammonia which was open to the atmosphere and the leg containing the washings was opened and cleaned. Finally the hydrazo compound was added and this leg resealed. After the seal had cooled, the other leg of the tube was removed from the liquid ammonia and allowed to warm to room temperature. The hydrazo compound was dissolved in ammonia and the solution poured over the nitride. The final reaction product was obtained by allowing all of the ammonia to evaporate from the tube, or by distilling the solvent into the opposite leg and cooling this leg in an open bath of ammonia. In either case the end of the tube was scratched with a file and broken off by means of a piece of hot glass.

The azo compounds were purified by recrystallization either from ligroin or liquid ammonia. Azobenzene and p-azotoluene are only slightly soluble in liquid ammonia at the temperature of an open bath of the liquid (about $-40°$).

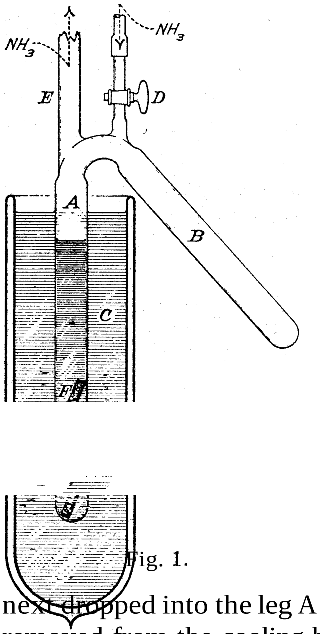

Fig. 1.

For those experiments in which iodine was used as the nitridizing agent, a two-legged reaction tube fitted with an addition tube was employed (Fig. 1). The tube was sealed up with the hydrazo compound in leg **A.** After distilling ammonia into the tube, leg A, was cooled in an open bath of liquid ammonia. With a stream of gaseous ammonia entering at D, the end of the addition tube, E, was cracked off with a bit of hot glass. Short pieces of glass tubing packed with the desired weight of iodine were next dropped into the leg A and tube E resealed.[13] After the tube had been removed from the cooling bath and allowed to warm to room temperature, the iodine slowly dissolved and reacted with the solution.[14]

The hydrazobenzene and *p*-hydrazotoluene used in this research were prepared by reducing the corresponding azo compound with zinc dust in a hot alcoholic alkaline solution[15] and recrystallizing from alcohol; m. p. of hydrazobenzene, 129°; *p*-hydrazotoluene, 124'. The values listed in the "International Critical Tables" are 131 and 126°, respectively.

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[13] Such a modification of the usual procedure is necessary because iodine liquefies in a stream of gaseous ammonia and forms a dangerously explosive mixture.

[14] This is the technique employed by Strain (Ref. 3), although not described fully by him.

[15] Gattermann, "Practical Methods of Organic Chemistry," translated by Schober and Babasinian, **3d** English ed frqm 11th German ed., 1928, p. 228.

Hydrazobenzene and Iodine.—To a solution of 0.2 g. of hydrazobenzene in liquid ammonia was added an excess of iodine. After all of the iodine had dissolved (three hours), the solution was cooled in an open-bath of liquid ammonia. The lowering of the temperature caused the separation of orange crystals (m. p. 68°). A mixture of equal quantities of these crystals and azobenzene fm. p. 68°) melted at 68°.

p-Hydrazotoluene and Iodine.—To an ammonia solution containing **0.14** g. of p-hydrazotoluene was added an excess of iodine. Overnight all of the iodine had disappeared and orange crystals had separated out. After washing three times with fresh ammonia, these crystals melted at 144°; when mixed with p-azotoluene, melting at 144°, the mixture melted at 144°.

Hydrazobenzene and Mercuric Nitride.—To the mercuric nitride prepared from **1.22** g. of the iodide was added **0.18** g. of hydrazobenzene in ammonia solution. At the end of two days, small globules of metallic mercury were visible in the bottom of the reaction tube. The ammonia-soluble product upon recrystallization from ligroin melted at 67.5°. An equal mixture of these crystals and azobenzene, melting at 68°, melted at **67.5".**

***p*-Hydrazotoluene** and Mercuric Nitride.—Two and one-tenth g. of mercuric iodide was converted to the nitride and treated with an ammonia solution containing **0.22** g of p-hydrazotoluene. At the end of two days finely divided mercury as well as a precipitate of p-azotoluene was visible in the tube. The latter product after extraction with ammonia and recrystallization from ligroin gave orange-yellow crystals which melted at 143°. A mixture of equal quantities of these crystals and those of *p*-azotoluene (m. p. **144")** melted at **143.5°**.

Hydrazobenzone and Bismuth Nitride.—To the bismuth nitride obtained from **1.32** g. of the iodide was added a solution containing **0.51** g. of hydrazobenzene. The mixture was allowed to stand for two days. The reaction product recrystallized from ligroin gave **0.483** g. of red crystals which melted at 67°; yield, 95%. A mixture of these crystals and an equal quantity of azobenzene melted at 67°.

Hydrazotoluene and Bismuth Nitride.—One and three-tenths grams of bismuth iodide and an excess of potassium were sealed in opposite legs of a reaction tube and ammonia distilled into the leg containing the iodide. During the subsequent distillation of ammonia from this leg into that containing the potassium small yellow needle crystals were observed in the iodide leg. Such a behavior indicates the probable existence of a moderately soluble ammono-basic iodide of bismuth.[16] The solution of *p*-hydrazotoluene remained in contact with the nitride for two days. On recrystallizing the reaction product from ligroin, orange-yellow crystals were obtained which melted at **143°**; a mixed melting point with p-azotoluene gave **143.5'.**

Hydrazobenzene as an Indicator.—In the legs of a three-legged reaction tube were sealed **0.5** g. of ammonium nitrate, a small amount of hydrazobenzene and **0.3** g. of potassium, respectively. After the conversion of the potassium to the amide, a drop of this solution was added to the yellow solution of hydrazobenzene. Immediately a reddish-brown color developed. Upon the careful addition of a drop of ammonium nitrate, the hydrazobenzene solution resumed its original yellow color. With the same sample of indicator, this process of discharging the color induced by bases was repeated several times.

Small amounts of hydrazobenzene and potassium hydroxide were sealed in a one-legged reaction tube and ammonia was distilled onto the mixture. The solution was colored dark brown.

***p*-Hydrazotoluene** as an Indicator.—A three-legged tube similar to the one de-

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[16] Franklin and Cady [Tars JOURNAL, 26, **512** (1904)] report a similar ammono-basic bismuth nitrate.

scribed abovr was charged with ammonium chloride, *p*-hydrazotoluene and potassium amide. The same induction and discharge of color were observed as in the case above.

Summary

1. Mercuric nitride and bismuth nitride have been shown to have the properties of nitridizing agents.

2. Hydrazobenzene and *p*-hydrazotoluene have been nitridized to the corresponding azo compounds in liquid ammonia solution using iodine, mercuric nitride and bismuth nitride.

3. Because of the formation of highly colored salts, both hydrazobenzene and hydrazotoluene may be used as sensitive acid-base indicators in liquid ammonia solutions.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE MONOPHENYL ETHERS OF GLYCERIC ACID

BY C. FREDERICK KOELSCH

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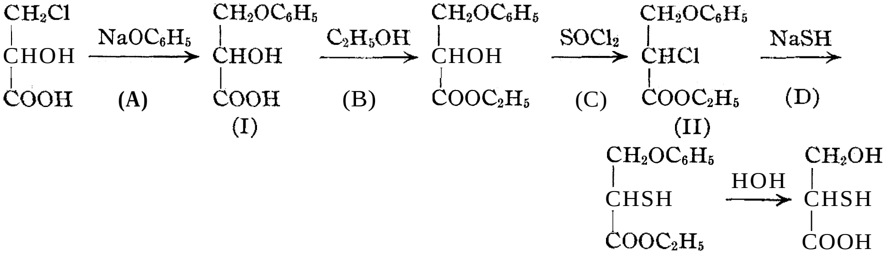
Investigations on the oxidation of β-thioglyceric acid, whose preparation was described in a previous paper,[1] showed the desirability of extending the study there outlined to the still unknown α-thioglyceric acid. It was considered feasible to attempt the preparation of this compound through the following reactions:



$$\begin{array}{c}CH_2Cl\\|\\CHOH\\|\\COOH\end{array}\xrightarrow[(A)]{NaOC_6H_5}\underset{(I)}{\begin{array}{c}CH_2OC_6H_5\\|\\CHOH\\|\\COOH\end{array}}\xrightarrow[(B)]{C_2H_5OH}\begin{array}{c}CH_2OC_6H_5\\|\\CHOH\\|\\COOC_2H_5\end{array}\xrightarrow[(C)]{SOCl_2}\underset{(II)}{\begin{array}{c}CH_2OC_6H_5\\|\\CHCl\\|\\COOC_2H_5\end{array}}\xrightarrow[(D)]{NaSH}\begin{array}{c}CH_2OC_6H_5\\|\\CHSH\\|\\COOC_2H_5\end{array}\xrightarrow{HOH}\begin{array}{c}CH_2OH\\|\\CHSH\\|\\COOH\end{array}$$

Reactions A, B and C were carried out successfully. Reaction D did not proceed as indicated; when ethyl α-chloro-β-phenoxypropionate (II) was treated with sodium hydrosulfide, a practically quantitative yield of phenol was obtained. The remainder of the reaction mixture was a black tar, the constituents of which are as yet unidentified. A study of this reaction is in progress.

This paper deals with the substances obtained in Reaction A. The reaction between p-chlorolactic acid and sodium phenoxide gave a satisfactory yield of β-phenoxylactic acid (I), but when the reaction mixture was worked over, it was found that this was not the sole product. Along

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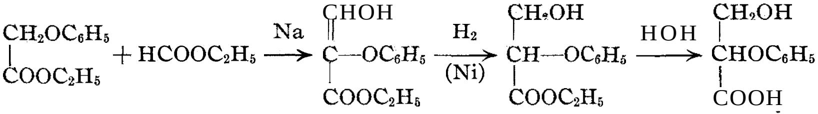
[1] Koelsch, THIS JOURNAL, 52, 1105 (1930).

with the β-phenoxylactic acid melting at 157.5–159°, there was obtained about 1% of a more soluble acid melting at 107–109°. The analysis and neutral equivalent of this compound indicated that it was isomeric with β-phenoxylactic acid.

On treatment with hydriodic acid, the low-melting acid gave phenol and β-iodopropionic acid, the same products which were obtained by a similar treatment of β-phenoxylactic acid. It seemed probable, therefore, that the low-melting compound was a-phenoxyhydracrylic acid (IV).

That the acid melting at 157.5–159° was the expected β-phenoxylactic acid was proved by converting it into the chloro ester (II) which was dehalogenated to give ethyl β-phenoxypropionate. The acid resulting from the hydrolysis of this ester was identified as β-phenoxypropionic acid by comparison with a sample prepared from β-bromopropionic acid.

That the acid melting at 107–109° was a-phenoxyhydracrylic acid was shown by its synthesis according to the following series of reactions



$$\begin{array}{l}CH_2OC_6H_5\\ |\\ COOC_2H_5\end{array} + HCOOC_2H_5 \xrightarrow{Na} \begin{array}{l}CHOH\\ \|\\ C{-}OC_6H_5\\ |\\ COOC_2H_5\\ \text{(III)}\end{array} \xrightarrow[(Ni)]{H_2} \begin{array}{l}CH_2OH\\ |\\ CH{-}OC_6H_5\\ |\\ COOC_2H_5\end{array} \xrightarrow{HOH} \begin{array}{l}CH_2OH\\ |\\ CHOC_6H_5\\ |\\ COOH\\ \text{(IV)}\end{array}$$

The reduction of formylphenoxyacetic ester (III) with zinc dust and acetic acid, with amalgamated zinc and acetic acid, or with amalgamated aluminum in neutral solution caused phenol to be eliminated from the molecule. The o-benzoate of the enol was unaffected by amalgamated aluminum. The reduction of the free enol was finally accomplished by using molecular hydrogen in the presence of catalytic nickel.

The first explanation for the formation of a-phenoxyhydracrylic acid which suggested itself was that the β-chlorolactic acid used was contaminated with a-chlorohydracrylic acid, and that the sodium phenoxide reacted with this to replace the halogen atom directly with the phenoxyl radical. Certain facts militating against this explanation may be brought forward. The β-chlorolactic acid[1,2] used was prepared from a-monochlorohydrin obtained by the action of hydrogen chloride on glycerol.[3] This monochlorohydrin subjected to the further action of hydrogen chloride gives a dichlorohydrin which has been shown to be nearly free of the α,β-compound.[4] Hence the monochlorohydrin used contained very little of the β-isomer, which would be the precursor of a-chlorohydracrylic acid. Although the above evidence does not preclude the possibility; that only 1%

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[2] The acid melting at 45–72" obtained from the oxidation was used without recrystallization. The unsharp melting point is considered to be caused by the presence of oxalic acid and, mainly, water.

[3] Conant and Quayle, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. II, p. 33.

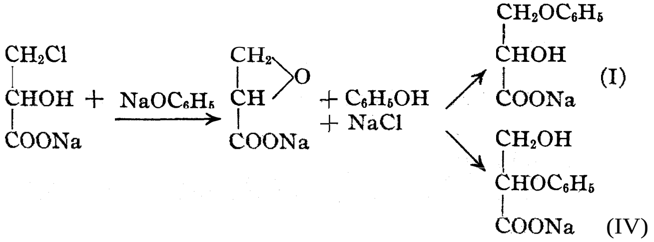
[4] Conant and Quayle, THIS JOURNAL, 45, 2771 (1923).

of a-chlorohydracrylic acid may be present, Melikoff's experiments indicate that this acid would yield β-phenoxylactic acid rather than α-phenoxyhydracrylic acid.

Melikoff[5] treated a-chlorohydracrylic acid with ammonia and was able to isolate only iso-serine, $CH_2NH_2—CHOH—COOH$, from the reaction mixture. He postulated that the α-chlorohydracrylic acid first lost hydrogen chloride, forming glycidic acid, which compound then added ammonia to form *iso*-serine.[6] Melikoff showed that glycidic acid added ammonia thus and considered this as evidence for the correctness of his assumed reaction mechanism.

According to the partition principle of Michael,[7] the addition of an unsymmetrical reagent to an unsymmetrical unsaturated compound (or ethylene oxide) gives rise to two isomers, the amount of each isomer thus produced being in proportion to the amount of chemical energy set free in its formation.

If a reaction mechanism analogous to that postulated by Melikoff is considered in the light of the partition principle, Reaction **A** may be formulated



This formulation appears to account most satisfactorily for the formation of both β-phenoxylactic acid and a-phenoxyhydracrylic acid in the reaction which is reported here.

Experimental

β-Phenoxylactic and a-Phenoxyhydracrylic Acids from β-Chlorolactic Acid.—A mixture of 600 g. of phenol, 400 g. of β-chlorolactic acid and a solution of 360 g. of sodium hydroxide in two liters of water was refluxed for two hours, acidified and the excess phenol removed by steam distillation. Cooling the solution gave crude β-phenoxylactic acid. The mother liquor contained β-phenoxylactic acid, a-phenoxyhydracrylic acid and sodium chloride, which were separated by evaporation and fractional crystallization. The a-phenoxyhydracrylic acid crystallized out only after the volume of the solution had been reduced to some 150 ml.

The crude β-phenoxylactic acid after treatment with charcoal, crystallized from water in colorless plates melting at 157.5–159° (uncorr.); yield, 400–425 g.

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.33; H, 5.49. Found: C, 59.35; H, 5.90. Mol. wt. (by titration). Calcd.: 182. Found: 185.5.

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[5] Melikoff, *Ber.*, 13, 1265 (1880).

[6] The same result has been obtained more recently with α-bromohydracrylic acid and ammonia [Neuberg and Mayer, Biochem. *Z.*, **3,** 119 (1907)].

[7] Michael, J. *prakt. Chem.*, [2] 60, 290 (1899).

A solution of the compound in concentrated sulfuric acid was colorless until warmed, when it became deep violet-red.

The crude α-phenoxyhydracrylic acid was separated from tarry impurities by extraction with hot toluene. It was finally crystallized from chloroform, from which solvent it was deposited in fine needles melting at 107–109°; yield, 3.8–6.0 g.

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.33; H, 5.49. Found: C, 59.00; H, 5.61. Mol. wt. (by titration). Calcd.: 182. Found: 183, 183.5.

TABLE I

DERIVATIVES OF α-PHENOXYHYDRACRYLIC AND β-PHENOXYLACTIC ACIDS

No.	Compound	Remarks	Yield, %
1	Methyl a-phenoxyhydracrylate[a]	Oil	69
2	Ethyl a-phenoxyhydracrylate[a]	Oil	71
3	α-Phenoxyhydracrylamide[b]	Needles fr. water	54
4	a-Phenoxyhydracrylanilide[c]	Needles fr. water	82
5	Silver a-phenoxyhydracrylate	Flat needles	..
6	Methyl β-phenoxylactate[a]	Oil	82
7	Ethyl β-phenoxylactate[a]	Fine needles fr. dil. alc.	74
8	β-Phenoxylactamide[b]	Plates fr. water	65
9	β-Phenoxylactanilide[c,e]	Plates fr. dil. alc.	85
10	Silver β-phenoxylactate	Fluffy plates	..

No.	B. p. or m. p. °C. (mm.) (uncorr.)	d^{25}_{25}	n^{25}_{D}	M_D Calcd.	Obs.
1	B. 168–169 (14)	1.1966	1.5213	49.92	49.90
2	B. 174–175 (16)	1.1545	1.5117	54 52	54.55
3	M. 137–139	....	....	...	...
4	M. 129–131[d]	....	....	...	...
6	B. 168–170 (17)	1.1934	1.5190	49.92	49.96
7	M. 71–72; (b. 173–175) (17)	....	....	...	...
8	M. 149–150	....	....	...	...
9	M. 122–123	....	....	...	...

		Calcd.			Found		
No.	Formula	C	H	N	C	H	N
1	$C_{10}H_{12}O_4$	61.2	6.12	..	60.9	6.19	...
2	$C_{11}H_{14}O_4$	62.8	6.67	..	62.7	6.44	...
3	$C_9H_{11}O_3N$	..	..	7.74	..	..	7.46
4	$C_{15}H_{15}O_3N$	..	..	5.46	..	..	6 56
5	$C_9H_9O_4Ag$	..	(Ag)	37.4	..	(Ag)	36.9
6	$C_{10}H_{12}O_4$	61.2	6.12	..	60 9	6.20	...
7	$C_{11}H_{14}O_4$	62 8	6.67	..	62 6	6.78	...
8	$C_9H_{11}O_3N$	..	..	7.74	..	..	7.54
9	$C_{15}H_{15}O_3N$	..	..	5.46	..	..	5.14
10	$C_9H_9O_4Ag$	..	(Ag)	37.4	..	(Ag)	37.4

[a] From the acid by the method of E. Fischer and Speier, Ber., 28, 3252 (1895), using hydrogen chloride. [b] From the methyl ester and concd. aqueous ammonia. [c] From the acid by heating for four hours at 190° with a slight excess of aniline. [d] Sintered at 122°. A mixture with an equal amount of @-phenoxylactanilide melted at 107–111°. [e] This compound could be obtained colorless for analysis only by crystallization from water, in which the colored impurities were insoluble. Four hundred ml. of boiling water was necessary to dissolve 0.4 g. of the substance; it was noted that all of the derivatives of β-phenoxylactic acid were much less soluble than the corresponding derivatives of a-phenoxyhydracrylic acid.

A solution of the compound in concd. sulfuric acid was colorless until warmed, when it became rose-red.

Reaction of β-Phenoxylactic and a-Phenoxyhydracrylic Acids with Hydriodic Acid.—Although heating β-phenoxylactic acid with hydrochloric acid or with hydrobromic acid gave only black resins, similar treatment with hydriodic acid gave substances which were characterized successfully. The solution resulting from heating 5 g. of β-phenoxylactic acid with 20 ml. of hydriodic acid (d 1.96) in a sealed tube at 120–125° for four hours was diluted with water, decolorized with sulfur dioxide, and extracted with ether. By washing this extract with sodium carbonate and sodium hydroxide, there were obtained 4.0 g. of a mixture of unchanged β-phenoxylactic acid and β-iodopropionic acid, and 1.4 g. of phenol (identified as phenyl benzoate). Since the mixture of acids could not be separated into its constituents by fractional crystallization, a portion (2.7 g) was heated for three hours at 180" with aniline (4.0 g.), giving a mixture of neutral β-phenoxylactanilide with basic β-anilinopropionanilide[8] which were easily separated. The latter compound was identified by analysis of its hydrochloride (calcd.: Cl, 12.84; found: Cl, 12.84) and by mixed melting points with the same compound prepared from β-bromopropionic acid and aniline.

The treatment of a-phenoxyhydracrylic acid (4.7 g.) with hydriodic acid was similar to that described immediately above. There were obtained 1.5 g. of phenol, and 3.4 g. of mixed acids. A hot benzene solution of a portion of the latter deposited a small amount of α-phenoxyhydracrylic acid (m. p. 95–100°; mixed m. p. 100–104°); the β-iodopropionic acid remaining in the benzene melted, after crystallization from warm water, at 80–81°. The remainder of the mixed acids was treated with aniline, the resulting anilides being separated and identified as before.

Esters of α-Chloro-β-phenoxypropionic Acid.—The general method of Darzens[9] for the replacement of the hydroxyl group with chlorine by the use of thionyl chloride and pyridine was applied successfully to the methyl and ethyl esters of β-phenoxylactic acid. The properties and analyses of the twice distilled esters are given in the accompanying table.

TABLE II

PROPERTIES AND ANALYSES OF ESTERS

No.	Ester	B. p., °C. (16 mm.) (uncorr.)	Yield, %	d_{25}^{25}	n_D^{25}
1	Methyl	153–154	77	1.2177	1.5166
2	Ethyl	165–167	55	1.1812	1.5091

No	M_D Calcd	M_D Obs	Pormula	Cl (Carius), % Calcd.	Cl (Carius), % Found
1	53 34	53 25	$C_{10}H_{11}O_3Cl$	16 53	16 41
2	57 94	57 77	$C_{11}H_{13}O_3Cl$	15 53	16 36, 16 65, 16 54[a]

[a] The third analysis of the compound was made on a sample purified by an additional distillation; the constants of this sample were identical with those measured for the twice distilled ester. The low yield and high chlorine content were probably caused by not cooling the mixture sufficiently during the addition of the thionyl chloride.

Dehalogenation of Ethyl α-Chloro-β-phenoxypropionate.—A mixture of 10 g. of ethyl α-chloro-β-phenoxypropionate, 20 g. of dry alcohol, 10 g. of acetic acid, 10 g. of zinc dust and a little copper carbonate was refluxed for eight hours. The mixture was then filtered and concentrated on a steam-bath. The addition of water precipitated an oil which distilled at 120–145° (15 mm.). A second distillation gave 3.4 g.

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[8] Cj. Autenrieth and Pretzell, *Ber.*, 36, 1262 (1903).

[9] Darzens, *Compt.* rend., 152, 1601 (1911).

of a halogen-free fraction boiling at 175–177" (50 mm.); d_{25}^{25} 1.0821; n_D^{25} 1.5055; M_D, calcd., 53.00; obs , 53.22. The boiling point of ethyl p-phenoxypropionate is reported to be 170° (40 mm.).[10]

The acid obtained by the hydrolysis of the ester with a mixture of equal weights of acetic acid, water and sulfuric acid melted alone or mixed with a sample of β-phenoxypropionic acid prepared from β-bromopropionic acid at 96–97° (uncorr). The melting point of this acid is reported to be 98°.[10]

Ethyl a-Phenoxy-p-hydroxyacrylate ("Formylphenoxyacetic Ester," III).—This compound was prepared by the method of Johnson and Guest[u] by the action of sodium on a mixture of ethyl formate and ethyl phenoxyacetate in ether. Contrary to the statement[12] that the compound could not be distilled under reduced pressure without decomposition, it was found that no decomposition took place when the distillation was carried out with the aid of an efficient water pump. This was shown by distilling the compound repeatedly, under which treatment the boiling point was not changed; the thrice distilled compound gave a benzoate identical with that obtained from the crude undistilled product. The following constants were observed: b. p., 148–150° (11 mm.); d_{25}^{25} 1.1637; n_D^{25} 1.5210; M_D calcd. (keto), 53.18; (enol), 54.13; obs., 54.43.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.46; H, 5.77. Found: C, 63.45; H, 5.83.

Benzoate.—This compound was prepared from the ester by the Schotten–Baumann reaction. It crystallized from dilute alcohol in fine needles which melted at 76–77°.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.24; H, 5.13. Found: C, 68.93; H, 5.11.

Ethyl a-Phenoxyhydracrylate from Ethyl Formylphenoxyacetate.—The oxymethylene compound was reduced in alcohol solution with hydrogen in the presence of catalytic nickel at a pressure of 150 atmospheres and at a temperature of 100°.[13] On distillation, the product boiled at 168–170° (10 mm.); d_{25}^{25} 1.1558; n_D^{25} 1.5125; M_D, calcd., 54.52; obs., 54.56; found: C, 62.50; H, 6.67. These constants agree well with those obtained for ethyl α-phenoxyhydracrylate prepared from β-chlorolactic acid (cf. Table I, No. 2).

The reagents usually employed for the reduction of oxymethylene compounds gave unsatisfactory results in the present instance. An ether solution of formylphenoxyacetic ester (10 g.) was treated with amalgamated aluminum according to the procedure described by W. Wislicenus.[14] From the ether solution there was obtained only phenol, which gave, on benzoylation, 8.0 g. of pure phenyl benzoate. The reduction of the oxymethylene compound in glacial acetic acid with zinc dust or amalgamated zinc led to a like result.

Phenoxyhydracrylamide (found: N, 7.49) prepared by ammonolysis of the ester was identical (mixed m. p.) with that obtained from p-chlorolactic acid (cf. Table I No. 3). Saponification of the ester gave the free acid (found: C, 59.01; H, 5.54) which melted at 109–110°; a mixture with an equal amount of the acid obtained from β-chlorolactic acid melted at 108–110°. The acid obtained by reduction gave a colorless solution in concd. sulfuric acid, which became yellow on warming. The color reaction and slightly low melting point of the acid prepared from β-chlorolactic acid are probably

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[10] Powell, THIS JOURNAL, **45,** 2708 (1923).

[11] Johnson and Guest, *Am. Chem. J.*,**42,** 285 (1909).

[12] Johnson and Heyl, *ibid.*, **37,** 636 (1907).

[13] This reduction was carried out by Professor Homer Adkins The procedure will be described in detail in a forthcoming paper. The author wishes to express his sincere appreciation to Professor Adkins.

[14] W. Wislicenus, Boklen and Reuthe, *Ann.*, **363,** 359 (1908).

caused by the presence of a small amount of β-phenoxylactic acid which could not be removed by fractional crystallization.

The assistance given by Professor S. M. McElvain during the course of this work is gratefully acknowledged.

Summary

The monophenyl ethers of glyceric acid, β-phenoxylactic acid and α-phenoxyhydracrylic acid, and a number of their derivatives have been prepared and characterized.

The possibility that both of these isomers may be formed simultaneously in the reaction between β-chlorolactic acid and sodium phenoxide has been pointed out.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 626]

THE INFLUENCE OF CERTAIN NEUTRAL SALTS UPON THE ACTIVITY OF MALT AMYLASE

BY H. C. SHERMAN, M. L. CALDWELL AND M. CLEAVELAND

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Recent work[1] has shown that pancreatic amylase not only is dependent for its activity upon the presence of electrolytes but that it differs markedly in its response in activity to the presence of different salts. In view of this fact and of the recent findings of several investigators[2] that the influence of electrolytes upon enzymic activity is dependent on several interrelated factors, it seemed of special interest to continue our studies of typical starch-splitting enzymes of plant and animal origin by ascertaining whether quantitative differences might also be obtained in the action of malt amylase by the presence or absence of certain salts when the other factors were very fully controlled in the light of all present knowledge. One phase of this work, that dealing with the influence of acetate and phosphate upon the activity of malt amylase, has already been described.[2] The results of the quantitative study of the influence of other salts upon the activity of malt amylase are reported briefly here.

Experimental

The general procedure employed in this investigation consisted in allowing the enzyme to act at 40° (±0.01°) for thirty minutes upon 2% starch solutions which differed among themselves with respect to either the salt content or the hydrogen-ion activity or both as explained below. At the

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[1] (a) Sherman, Caldwell and Dale, THIS JOURNAL, 49, 2596 (1927); (b) Sherman, Caldwell and Adams, *ibid.*, 50, 2529, 2535, 2538 (1928).

[2] Sherman, Caldwell and Boynton, *ibid.*, 52, 1669 (1930), and references therein contained.

expiration of this half-hour period, the extent to which the starch had been converted to reducing sugars, mainly maltose,[3] was established according to the gravimetric method previously described[4] and this was taken as the measure of the relative activity of the enzyme.

The hydrogen-ion activities of the substrates were adjusted by mixtures of sodium acetate and acetic acid, present in a total concentration of 0.01 M acetate. Such mixtures had been shown[2] to be satisfactory for work with this enzyme. By changing the proportions of equimolar sodium acetate and acetic acid, it was possible to adjust the solutions to different desired hydrogen-ion activities without changing the total concentration of acetate. The total concentration of 0.01 *M* acetate was chosen for several reasons. It had been found to afford the desired buffer effect and at the same time was low enough not to interfere with the study of the influence of other salts. Previous work had also shown[2] that acetate as well as phosphate exerts a very slight favorable influence upon malt amylase. This influence, in the case of acetate, is practically constant through a wide zone of concentrations including 0.01 M, which is therefore a suitable concentration to use. The hydrogen-ion activities of all solutions were measured electrometrically. In all of the experiments here reported, the conditions of time, temperature and the concentrations of starch, enzyme and total acetate were constant.

As regards the factors which were varied, the plan of the work was as follows: (1) in order to determine whether or not sodium chloride has any influence upon the activity of malt amylase, direct comparisons were made of the enzymic activity (a) at graded hydrogen-ion activities in the presence and absence of the salt at fixed concentrations, and (b) in the presence of graded concentrations of the salt at fixed hydrogen-ion activities. (2) The other neutral salts studied, potassium chloride, sodium nitrate and sodium sulfate, were compared in a similar manner as to their effect upon the hydrolysis of starch with malt amylase. The enzymic activity in the presence of these salts at a single concentration and hydrogen-ion activity was compared with that exerted in the absence of salt both at the same hydrogen-ion activity and at the optimal hydrogen-ion activity for the enzyme and conditions here employed. (3) Finally, the effect of different concentrations of each salt upon the activity of malt amylase was established at each of three hydrogen-ion activities: (a) at the optimum, (b) on the alkaline side of the optimum, (c) on the acid side of the optimum.

A dry preparation of malt amylase, purified from dialyzed malt extract according to a modification of the method described by Sherman and Schlesinger,[5] was used.

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[3] Sherman and Punnett, THIS JOURNAL, 38, 1877 (1916).

[4] Sherman and Walker, *ibid.*, 43, 2461 (1921).

[5] Sherman and Schlesinger, *ibid.*, 37, 643 (1915).

All reagents were carefully purified. The salts were of the highest purity obtainable and were recrystallized three times in all cases with the exception of sodium chloride, which was prepared and purified by the method of Richards and Wells.[6] Soluble starch which constituted the substrate was washed repeatedly and air dried. Redistilled water was used for all solutions.

Results with Sodium Chloride.—Parallel measurements of the activity of the enzyme in the presence of 0.01 *M* sodium chloride and in its absence, each at closely graded hydrogen-ion activities from PH 4.0 to PH 6.2, showed that the enzymic activity was greater in the presence of the sodium chloride in the more acid solutions, PH 4.3 to PH 4.0, and in the more alkaline solutions, PH 5.1 to PH 6.2. In solutions of intermediate reaction from approximately PH 4.3 to PH 5.1, however, the presence of sodium chloride had no appreciable influence upon the activity of the enzyme. These solutions correspond approxiniately to the optimal hydrogen-ion activity previously established[2] for this enzyme in the presence of this concentration of acetate. Similar results were obtained in a series of experiments with 0.02 M sodium chloride. Thus sodium chloride in concentrations of 0.01 and 0.02 M did not increase the activity of the enzyme at the optimal, but rendered it more active in solutions of less favorable, hydrogen-ion activity.

This was also found to be true when, in another series of experiments, the influence of several concentrations of sodium chloride (0.01, 0.02, 0.05, 0.07 and 0.10 *M*) was carefully and repeatedly measured: at the optimal hydrogen-ion activity (PH 4.5), in solutions more acid (PH 4.0) and in solutions less acid (PH 5.5).

At its optimal hydrogen-ion activity, the enzyme was as active without as with the sodium chloride; but the presence of this salt helped to overcome the retarding influence of an unfavorable hydrogen-ion activity upon the action of the enzyme.

This was demonstrated for all of the five concentrations of sodium chloride tested (0.01 to 0.10 M), the lower concentrations of the salt appearing more favorable on the acid, and the higher concentrations on the more alkaline side.

If the activity of the enzyme at its optimal hydrogen-ion activity (PH 4.5) be taken as 100%, its activity at PH 4.0 was 89% without added salt and 99% with 0.01 M sodium chloride; while at PH 5.5 the activity of the enzyme was 77% without neutral salt and 97% with 0.10 M sodium chloride.

Thus malt amylase showed a practically optimal action through a wider range of hydrogen-ion activity when sodium chloride was present in suitable concentration than it did in the absence of the salt.

Results with Potassium Chloride.—The influence of potassium chloride

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[6] Richards and Wells, THIS JOURNAL, 27, 459 (1905).

was studied in the same way as that of sodium chloride and with nearly the same results. The differences between the data obtained with these two salts were no greater than might reasonably be allowed for experimental error, but the average activity of the enzyme was in most cases slightly higher in the presence of the potassium, than of the sodium, salt.

Results with Sodium Sulfate.—At the optimal hydrogen-ion activity, P_H 4.5, the average enzymic activity was slightly higher in the presence of 0.01 M to 0.10 M sodium sulfate than in its absence, but here again, as in the case of potassium chloride, the differences were so small as to be of doubtful significance. At hydrogen-ion activities on either side of the optimum, (*viz.*, P_H 4.0 and P_H 5.5, respectively) the activity of the enzyme was increased by the presence of the sulfate (0.01 to 0.10 M), but this favorable influence was less than that exerted by the same concentrations of sodium or potassium chloride under the same conditions and decreased with increasing concentrations of the salt in solutions on the acid side of the optimum.

Results with Sodium Nitrate.—Sodium nitrate was found to have a less favorable influence upon the activity of malt amylase than the same concentrations of sodium or potassium chloride when tested under the same conditions.

Summary and Conclusions

The influence of sodium chloride, potassium chloride, sodium sulfate and sodium nitrate upon the saccharogenic activity of malt amylase has been investigated and special consideration has been given to the influence of changes in hydrogen-ion activity and salt concentration.

Under the experimental conditions here described, neutral salts are not essential to the activity of malt amylase nor do they increase the saccharifying action of the enzyme above that shown in their absence at the optimal hydrogen-ion activity.

The activity of malt amylase was increased at unfavorable hydrogen-ion activities by the presence of these salts, but not to the same extent by different salts. Those studied here may be arranged according to the decreasing magnitude of their effect upon the activity of the enzyme at unfavorable hydrogen-ion activities as follows: sodium and potassium chlorides, sodium sulfate, sodium nitrate.

In solutions of unfavorable hydrogen-ion activity, the addition of sodium chloride in the concentrations most favorable to the action of the amylase (0.01 M at P_H 4.0 or 0.10 M at P_H 5.5) restored the enzyme to an activity practically equal to that obtaining in the absence of salt at the optimal hydrogen-ion activity, P_H 4.5. Thus with the addition of the proper amount of sodium chloride, malt amylase exerts its highest activity in solutions differing more widely in hydrogen-ion activity than in its absence.

The findings here reported explain the contradictory evidence presented by various workers from time to time regarding the influence of salts upon the activity of this enzyme and emphasize anew the importance of controlling the hydrogen-ion activities of the solutions in which the enzyme action occurs.

The influence of salts upon the activity of malt amylase appears to be specific.

These findings as a whole establish quite definitely a difference, in dependence of optimal activity upon neutral salts, between pancreatic and malt amylases, which are being studied in detail as representative and analogous enzymes of animal and plant origin, respectively.

NEW YORK CITY

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES, ELI LILLY AND COMPANY]

DIALKYL BARBITURIC ACIDS

BY H. A. SHONLE, ANNA K. KELTCH AND E. E. SWANSON

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Nearly a hundred different 5,5-disubstituted barbituric acid derivatives have been prepared in the quarter of a century since Fischer and Dilthey[1] and Fischer and von Mering[2] found that certain of these derivatives could be used therapeutically as sedatives and hypnotics. These investigators were aware that certain of the compounds were more active as hypnotics than others and that the effect could be markedly changed by varying the chemical nature of the substituent radical.

Subsequent investigations[3] have shown that those barbituric acids in which the sum of the C atoms in the two substituent groups is 6, 7 or 8 are the most effective. When evaluated on rats, cats, rabbits or mice, by the intravenous or subcutaneous injection of their sodium salts, this group shows, in most instances, a wider margin of safety between the anesthetic or down dose and the toxic dose than does, for example, diethylbarbituric acid.

The investigation was started in 1927 for the purpose of studying the various isomeric amyl-ethyl and amyl-allyl derivatives of the barbituric acids because of the commercial availability of certain of the amyl alcohols, and to extend the study of the secondary alkyl-ethylbarbituric acid series.[4]

[1] Fischer and Dilthey, *Ann.*, 335, 334 (1904).

[2] Fischer and von Mering, *Therap. d. Gegenwart.*, 44, 97 (1903); 45, 145 (1904).

[3] (a) Carnot and Tiffeneau, *Compt. rend.*, 175, 242 (1922); (b) Shonle and Moment, THIS JOURNAL, 45, 243 (1923); (c) Volwiler, *ibid.*, 47, 2236 (1925); (d) Nielson, Higgens and Spruth, *J. Pharmacol.*, 26, 371 (1926); (e) Swanson and Page, *ibid.*, 31, 1 (1927); (f) Dox and Hjort, *ibid.*, 31, 455 (1927).

[4] (a) During the course of this investigation Dox and Jones, THIS JOURNAL, 50, 2033 (1928), have reported on 5-n-amyl-5-ethylbarbituric acid. (b) Volwiler and Tabern described a number of amyl-ethyl and amyl-allyl derivatives at the Minneapolis Meet-

In view of Hsueh and Marvel's[5] statement relative to *sec.*-butylethylbarbituric acid we carefully repeated our work and found that this acid does not melt at 197°, as stated by them, but that after repeated crystallization *sec.*-butyl-ethylbarbituric acid melted at 164–165° (corr.). Our former figure[3b] of 158° (uncorr.) had been obtained with a limited amount of substance.[6]

In repeating this former work of ours we found that if we introduced the *sec.*-butyl group in ethylmalonic ester, we obtained a satisfactory yield of *sec.*-butylethylmalonic ester, which yielded *sec.*-butylethylbarbituric acid melting at 164°. However, if we reversed the procedure, we were able to introduce but an insignificant amount of the ethyl group into the *sec.*-butylmalonic ester, and could not separate any of the diethyl *sec.*-butylethylmalonate by fractional distillation. The barbituric acid prepared from the higher-boiling fraction of the ester was physiologically inert, melted at about 190° and proved on analysis to be *sec.*-butylbarbituric acid contaminated with a trace of *sec.*-butylethylbarbituric acid. It was possible to introduce the allyl group into this *sec.*-butylbarbituric acid, *sec.*-butylallylbarbituric acid having the correct melting point being obtained on recrystallization.

It was likewise found impossible to introduce the ethyl group into the *sec.*-amyl- or the cyclopentylmalonic esters or the allyl group into *sec.*-butylmalonic ester. To all outward appearance the reaction was normal, sodium bromide being deposited as usual. The reaction occurred, however, between the aliphatic bromide and the sodium ethylate instead of between the aliphatic bromide and the sodium *sec.*-butylmalonic ester, which indicates that the equilibrium was displaced toward the sodium ethylate since it reacted with the alkyl bromide. This may be interpreted as an instance of steric hindrance, or as an instance of the difference in the negativity of the secondary aliphatic substituted as compared to the primary aliphatic substituted malonic esters.

Experimental

Alcohols.—In view of the improbability of successfully purifying the commercial *sec.*-amyl alcohols by fractionation, the synthetic *sec.*-amyl alcohols prepared by the Grignard method at the Eastman Kodak Laboratories were used. Di-*n*-propylcarbinol and methylbutylcarbinol were likewise obtained from the same source. Cyclo-

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ing of the American Chemical Society, September, **1929**, This Journal, **52**, 1676 (1930), including propylmethylcarbinyl- and *sec.*-butylcarbinyl-ethylbarbituric acids and the esters from which they were prepared.

[5] Hsueh and Marvel, *ibid.*, 50, 855 **(1928)**.

[6] Dr. Marvel was kind enough to send us a sample of his acid and the ester from which it was prepared. Investigation showed that the 197° melting acid was almost physiologically inert, and analyzed as *sec.*-butylbarbituric acid which melts at 197°. The ester had a boiling point and refractive index much closer to dietbyl *sec.*-butylmalonate than to diethyl *sec.*-butylethylmalonate.

pentanol was prepared by reducing, in the presence of a platinum catalyst,[7] cyclopentanone obtained from adipic acid.[8] The other alcohols, obtained from various sources, presented no unusual aspects.

Alkyl Bromides.—The primary alkyl bromides were prepared according to the method of Kamm and Marvel,[9] while the secondary alkyl bromides were prepared by the Norris[10] method.

When the work was initiated, the authors had not considered that rapidly distilling a secondary alcohol with hydrobromic acid would produce other than the corresponding bromide in a degree of purity satisfactory for synthetic work. It was noted at that time, however, that the malonic esters and barbituric acids prepared from 2-bromo- and 3-bromopentane which had been made by the above method had similar physical characteristics. Dr. M. S. Kharasch, in discussing these reactions with one of us, pointed out that even rapidly distilling either of the 2 or 3-pentanols with hydrobromic acid should result in a rearrangement tending to give the same equilibrium mixture of 2 and 3-bromopentane, the exact proportions of the isomers depending on the conditions of the reaction.

We were later informed of the quantitative determination made by Dr. Sherrill and her co-workers,[11] now published, in which the values of the D line of 2-bromopentane and 3-bromopentane were shown to be at 20°, 1.4412 and 1.4443, respectively. Since Lucas, Simpson and Carter[12] have shown that there is a linear relation between the composition and refractive index, one can determine by calculation that the bromide obtained by Sherrill from diethylcarbinol and hydrobromic acid was a mixture of 71% 2-bromopentane and 29% 3-bromopentane, while that obtained from propylmethylcarbinol was a mixture of 81% 2-bromopentane and 19% 3-bromopentane.

It is evident that the preparation of *sec.*-amyl bromides by the usual methods results in mixtures and this circumstance doubtless obtains for the higher secondary bromides. In order to be sure then of the homogeneity of secondary bromides, one should use the method of Kharasch as described in detail by Sherrill, which gave as judged by the refractive index a 2-bromopentane slightly purer than that obtained by Lucas and Moyse.[13]

When the bromopentane obtained by rapidly distilling propylmethylcarbinol with 48% hydrobromic acid was washed and dried as directed by Sherrill, and fractionated,

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[7] Adams, Voorhees and Shriner, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1928,** Vol. VIII, p. 92.

[8] Thorpe and Kon, *ibid.,* **1925,** Vol. V, p. 37.

[9] Kamm and Marvel, *ibid.,* **1921,** Vol. *I*, p. 1.

[10] Norris, ***Am. Chem. J.,*** 38, 626 (1907); THIS JOURNAL, **38,** 1075 (1916); McCullough and Cortese, *ibid.,* **51,** 225 (1929).

[11] (a) Sherrill, Otto and Pickett, ibid., **51,** 3023 (1929); (b) Sherrill, Baldwin and Haas, *ibid.,* **51,** 3034 (1929).

[12] Lucas, Simpson and Carter, *ibid.,* **47,** 1462 (1925).

[13] Lucas and Moyse, *ibid.,* **47,** 1459 (1925).

two main cuts were obtained, one boiling at 117–118°, having a refractive index n_D^{20} 1.4416, the other boiling at 118–118.5°, with a refractive index n_D^{20} 1.4418, corresponding, respectively, to 87 and 81% of 2-bromopentane. In another trial, a 118–119° cut from technical propylmethylcarbinol was used. The two main cuts of the bromide boiled at 116.5–117°, with a refractive index n_D^{20} 1.4413, and 117–117.5°, with a refractive index n_D^{20} 1.4415, corresponding, respectively, to 97 and 90% of 2-bromopentane.

On distilling diethylcarbinol with 48% hydrobromic acid, a bromopentane is obtained which on fractionating gave a main fraction boiling at 117°, with a refractive index n_D^{20} 1.4433, corresponding to 68% of 3-bromopentane. However, when diethylcarbinol, obtained from technical alcohol, was used, the resulting bromides could be separated into two main fractions, one boiling at 115–116°, having a refractive index n_D^{20} 1.4419, and the other boiling at 116–117°, having a refractive index n_D^{20} 1.4425, corresponding, respectively, to 77 and 58% of 2-bromopentane.

This explains then why malonic esters prepared from these secondary alkyl bromides had a wider range of refractive indices and boiling points than did the malonic esters containing primary alkyl groups. Since the *sec.*-hexyl and -heptyl bromides used in this research were prepared in an analogous manner, similar rearrangements may have occurred.

When isopropylmethylcarbinol is distilled from 48% hydrobromic acid, the distillate is a mixture of amylene, *tert.*-amyl bromide and some 2-bromo-3-methylbutane.[14]

Mono-alkyl Malonic Esters.—The usual methods of preparing the mono-alkyl substituted malonic esters were employed,[15] no marked differences being observed in the yields from the primary and secondary aliphatic bromides. In actual practice it is unnecessary to use an amount of alcohol more than 10 times the weight of the sodium. The yields of the mono-substituted esters were generally greater than of the corresponding disubstituted esters and the reaction was completed in less time.

Dialkyl Malonic Esters.—The usual method of preparing the disubstituted malonic esters was employed when primary bromides were used. The use of iso-amyl chloride instead of iso-amyl bromide in the preparation of diethyl iso-amylethylmalonate did not lower the yield. When the *sec.*-amyl or -hexyl bromides were used the yields by the above methods were quite low, although the secondary group was introduced last. If, however, most of the alcohol was removed from the sodium salt of the mono-substituted ester before the bromide was added, the yields were bettered.

Diethyl hydroxyethylethylmalonate was obtained in a 27% yield when ethylene chlorohydrin was caused to react in the usual manner with sodium diethyl ethylmalonate. In contrast to diethyl hydroxyethylmalonate, it can be distilled under vacuum without decomposition. A better yield would undoubtedly be obtained if benzene were used in place of the alcohol.

Mono-substituted Barbituric Acids.—The mono-substituted barbituric acids were prepared by condensing the mono-substituted malonic esters with urea in absolute alcohol in the presence of sodium ethylate,[1] gently reflusing for two to three hours. Too prolonged refluxing causes a poor yield. They were isolated and purified in the usual manner.

Disubstituted Barbituric Acids.—Certain of the allyl-alkyl barbituric acids were prepared by the interaction of allyl bromide on the sodium salt of the desired mono-

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[14] Wischnegradsky, ***Ann.***, 190, 328 (1878), obtained tertiary halides instead of secondary halides on treating isopropylmethylcarbinol with aqueous hydrochloric and hydriodic acids at 40°.

[15] Adams and Kamm, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1924, Vol. IV, p. 11.

substituted barbituric acid[16] The most satisfactory yields were obtained when the barbituric acid was dissolved in a molecular quantity of 25 to 35% aqueous potassium hydroxide, to which was added somewhat in excess of a mole of allyl bromide and alcohol to about 10% of the total volume. The reaction was carried out in a shaking machine, from forty to fifty hours' time being required. Without the alcohol the reaction proceeded more slowly. The disubstituted acids were isolated and purified in the usual manner.

Most of the disubstituted barbituric acids were prepared by Fischer's method with the exception that a prolonged refluxing in a boiling water bath or on the sand-bath advantageously replaced the briefer period of heating in an autoclave. In some instances, after refluxing for one hour, most of the alcohol was removed under vacuum and the solid residue was heated in a boiling water-bath for four hours.

Technique.—In carrying out the fractional distillation under vacuum it was found that the refractive index was a better measure of purity than the pressure and boiling point. Consequently fractionation was repeated until a middle portion having a constant refractive index (or relatively constant in the instance of esters having a secondary group) was obtained.

The refractive indices were determined with an Abbé refractometer, with the temperature held constant to 0.2°. Duplicate observations taken on different days checked within one point in the fourth place.

The fractional distillation was carried out with the Fischer and Harries[17] apparatus which permits the fractionation to proceed while samples are being removed. Instead of the Claisen flask, a 200- or 500-cc. round-bottomed pyrex flask was used to which was attached a 30-cm. column.[18] The temperature was recorded by an Anschütz thermometer, the stem of which was entirely contained within the top of the fractioning column. During the course of the fractional distillation, even though the temperature was constant, repeated small cuts were made in order to obtain more data on the refractive index of the distillate.

No attempt was made to obtain the ultimate analysis of the esters since they were to be used as intermediates. The constancy of boiling point and refractive index served as the basis for making the cuts. Two or more preparations of each of the esters and barbituric acids have been made during the course of this investigation.

The mono- and disubstituted malonic esters prepared are given in Tables I and II. The yields are reported only for the ester having the described physical properties. In every instance refractionation of the lower cuts would have increased the yield.

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[16] (a) Volwiler, THIS JOURNAL, 47, 236 (1925); (b) Preiswerk, U. S. Patent 1,444,802 (1923); (c) Dox, U. S. Patent 1,615,870 (1927).

[17] Fischer and Harries, *Ber.*, 35, 2158 (1902).

[18] This column had an internal diameter of 2 cm. and is indented as described in THIS JOURNAL, 39, 2718 (1917).

TABLE I

MONO-SUBSTITUTED MALONIC ESTERS

Diethyl malonate derivatives	Yield, %	Boiling point °C.	Mm.	D
β-Hydroxyethyl[a]	8.3	136–137	15	1.4312[b]
Sec.-butyl[3a]	50.8	94–95	3	1.4248
n-Amyl[3]	44	121–123	6	1.4253
Iso-amy1[3"]	54.4	102	3	1.4255
Diethylcarbinyl	35.5	100–102	3	1.4276
Propylmethylcarbinyl[c]	50.5	103–104	4	1.4273
Cyclopentyl	56	113.8	4	1.4434

[a] Traube and Lehmann, *Ber.*, 32, 720 (1899), first described this ester. Cretcher, Koch and Pittenger, THIS JOURNAL, 47, 3083 (1925), were unable to distil hydroxyethylmalonic ester prepared from ethylene oxide and malonic ester without decomposition. We treated an absolute alcoholic solution of 1 mole of the sodium salt of malonic ester with 1.05 moles of ethylene chlorohydrin in the usual manner. The low yield obtained was due both the fact that most of the malonic ester had not entered into the reaction and that decomposition occurred during the fractionation. [b] Refractive index at 25°. [c] Boedecker, U. S. Patent 1,739,662, gives 122–125° at 13 mm.

TABLE II

DISUBSTITUTED MALONIC ESTERS

Diethyl malonate derivatives	Yield, %	Boiling point °C.	Mm.	n^{20}_D
n-Butyl-allyl	**80**	127–131	11–12	1.4387
Sec.-butyl-ethyl[3b]	39	100–103	3.5–4	1.4329
β-Hydroxyethyl-ethyl	27	128–131	6	1.4444
n-Amyl-ethyl[3]	39.7	136.5	10	1.4295[a]
Iso-amyl-ethyl[3b]	41	130.5	10	1.4295
Sec.-butylcarbinyl-ethyl[4b]	29.8	141–143	15	1.4316
Propylmethylcarbinyl-ethyl[4b]	27	111–112.5	4	1.4343
Diethylcarbinyl-ethyl	20	110–112	4	1.4329–1.4337[a]
Isopropylmethylcarbinyl-ethyl	10	110–116	7	1.4400[a]
Cyclopentyl-ethyl	48	115.4–116 2	4	1.4448
n-Butylmethylcarbinyl-ethyl	33–43	126–134	9	1.4331–1.4366[a]
Di-n-propylcarbinyl-ethyl	31	127–133	10	1.4302
Phenylethyl-ethyl	39	173–177	5	1.4829–1.4836[a]
n-Heptyl-ethyl	62	1435	3 5	1.4343

[a] Refractive index at 25°.

Boiling Points.—The following boiling points were observed: for diethyl ethylmalonate, 92.2" at 10 mm., 106° at 19 mm., 115.5' at 30 mm , 121" at 40 mm.; for diethyl iso-amylethylmalonate, 121.5° at 6 mm., 130.5° at 10 mm., 143.5° at 20 mm., 154° at 30 mm.; for diethyl iso-amylmalonate, 104.4" at 4 mm., 119.5° at 8 mm., 125.5° at 10 mm., 137.5" at 19 mm. and 146.5" at 29 mm.

Tables III and IV describe the mono- and disubstituted barbituric acids prepared from the above described esters.

Isopropylmethyl~rbinyl-ethylbarbituric acid was prepared in the usual manner from the corresponding malonic ester in an exceedingly low yield. It melts at 183–186° and is physiologically active. An amount of the barbituric acid sufficient for analysis and complete pharmacological testing was not prepared.

The di-n-propylcarbinyl-ethylbarbituric acid prepared gave a nitrogen value al-

TABLE III

MONO-SUBJTITUTED BARBITURIC ACIDS

Barbituric acid derivative	Yield, %	Melting point, °C. (corr.)	Nitrogen, % Calcd.	Found	
Propylmethylcarbinyl"	76	164–166	14.14	14.47	14.33
Diethylcarbinyl[b]	69	165–168	14.14	14.58	14.63
Cyclopentyl	51	221–223	14.29	13.97	13.95

[a] Boedecker, U. S. Patent 1,739,662 gives 162–163°, corr. [b] German Patent 293,163 describes a diethylcarbinyl barbituric acid having a melting point of 198°.

TABLE IV

DISUBSTITUTED BARBITURIC ACIDS

Barbituric acid derivative	Yield, %	Melting point, °C. (corr.)	Nitrogen, % Calcd.	Found	
Propylmethylcarbinyl-ethyl[a]	52	128.5–130	12.39	12.50	12.59
Diethylcarbinyl-ethyl"	36	127–129	12.39	12.00	11.88
Sec.-butylcarbinyl-ethyl[4b]	54 5	136–138	12.39	12.57	12.59
Cyclopentyl-ethyl	73	182–183	12.50	12.40	12.48
n-Butylmethylcarbinyl-ethyl	42	121–123	11.66	12.17	1208
β-Hydroxyethyl-ethyl[b]	67	178	...	....	
Propylmethylcarbinyl-allyl	50	86–88	11.76	12.01	12.04
Diethylcarbinyl-ally1	..	Wax-like	11.76	....	
Cyclopentyl-allyl	23	161–163	11.86	11.63	11.58
n-Butyl-allyl[c]	58	125–125.5	...	....	

[a] German Patent 293,163 describes both of these barbituric acids but gives a melting point of 162° for the diethylcarbinyl-ethylbarbituric acid. [b] It was found possible to prepare the β-hydroxyethyl-ethylbarbituric acid in the usual manner from diethyl hydroxyethylmalonate. Cretcher, Koch and Pittenger, THIS JOURNAL, 47, 3083 (1925), using an indirect method, obtained a melting point of 176" (corr.) for this acid. [c] Prepared from diethyl n-butyl-allylmalonate instead of by the action of allyl bromide on potassium n-butylbarbiturate, as described by Volwiler.[3c]

most 1% above the theoretical and melted around 158°. An acid melting about 10° lower was also obtained; both were physiologically active.

n-Butylmethylcarbinyl-ethylbarbituric acid. When the crude acid was recrystallized from a benzene–gasoline solution and then from dilute alcohol, two fractions were obtained; the major fraction melted at 122.5°, and had 12.08 and 12.17% of nitrogen, while the minor fraction melted at 106° and had 11.70 and 11.95%. Both were equally effective as hypnotics. The higher-melting product is presumed to be the *n*-butylcarbinyl-ethylbarbituric acid isomer.

Discussion

The disubstituted barbituric acids described are readily soluble in hot benzene (in contrast to the slight solubility of the mono-substituted) and can be crystallized from benzene or dilute alcohol. The one exception was the diethyl-allylbarbituric acid which precipitated as an oil, hardening on standing. These barbituric acids are almost insoluble in water, but dissolve readily in dilute sodium hydroxide solutions.

That the aqueous solutions of the alkali metal salts of the disubstituted barbituric acids are not indefinitely stable does not seem to be generally recognized outside of the chemical laboratory. Solutions of some of these salts show evidences of decomposition after a few days' standing. When a 5 or 10% solution of the sodium salt is boiled but for a short time, the ring is ruptured and ammonia is evolved. After a more prolonged boiling, a solid separates out as the solution cools. In the case of sodium iso-amyl-ethylbarbiturate, this solid was shown to be iso-amyl-ethylacetylurea. The amount of the precipitate which occurs after boiling an aqueous solution is not a measure of the full extent of the ring cleavage.

Initial decomposition can be detected by slowly adding a 1:10 solution of hydrochloric acid to the cold solution of the sodium barbiturate until the precipitation of the barbituric acid is complete, filtering off the precipitate, washing it with water and drying for a few hours at 70 and 80°. If there has been any decomposition the melting point will be lower than that of the pure barbituric acid initially used to prepare the salt. Since the difference may be only a few degrees, the melting points of the control and the test sample should be run at the same time.

It is essential in preparing solutions for biological study that any excess of alkali over one molar proportion should be avoided, that only a minimum amount of warming should be employed, and that only freshly prepared solutions be used.

Various salts of ammonia, mono-alkyl- and dialkylamines were prepared by dissolving the above-described barbituric acids in an excess of a solution of the volatile base and then evaporating the excess of the base and solvent until the solid salt was obtained. It was found that unless the salt was protected from exposure to air, the loss of the volatile base continued, leaving a mixture of the barbituric acid and the salt which was not water soluble.[19]

The addition of alcohol or glycerin to aqueous solutions of the various sodium barbiturates lessens the rate of decomposition. If, further, a weak organic acid is added to just short of the point of precipitation, the stability is further increased because of the lowering of the alkalinity. In this way solutions of the salts of more labile barbituric acids may be stabilized for some months. An absolute alcoholic solution of a sodium barbiturate does not decompose on boiling. The different barbituric acids exhibit varying rates of decomposition under the same conditions, those with a greater molecular weight usually being the more readily decomposed.

The alkali metal salts are best prepared by concentrating under vacuum non-aqueous solutions of equimolar proportions of the alkali metal hydrox-

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[19] Kubli, U. S. Patent 1,316,047, has prepared various alkylamine salts of barbituric acids with the expectation of overcoming the decomposition caused by the strong alkaline solution of the sodium salts. We have observed that the ampouled solution of Somnifen, an alkylamine salt of allyl-isopropylbarbituric acid, has decomposed in standing, forming the usual alkali-insoluble precipitate.

ide and the barbituric acid until the salt is obtained in solid form. The alkali metal salts of the barbituric acids of higher molecular weight are more hygroscopic than those of a lower molecular weight.

The calcium and magnesium salts are less soluble than the sodium, potassium or lithium salts, and may be prepared by adding the calculated amount of a soluble salt of the desired alkaline earth metal to a solution of the sodium barbiturate, and concentrating until a precipitate of the alkaline earth barbiturate occurs.[20]

No attempt will be made to report extensive pharmacological data, nor will any theory be advanced as to the mode of action of the barbituric acids. However, the exceedingly prompt effect following intravenous injections of solutions of their sodium salts and the relatively delayed appearance of unchanged barbituric acid in the urine are presumptious of the functioning of the intact molecule.

The effective and fatal doses were obtained by injecting intraperitoneally into white rats freshly prepared 2% solutions of the sodium salts of the various barbituric acids. Animals of about 100 g. weight, which had been starved for twenty-four hours previous to the injection, were used. The effective dose reported (M. E. D.) is that amount which will abolish reflexes when the inner ear is touched with a thin wooden applicator. (This depth of anesthesia is not sufficient to permit indiscriminate operative procedures to be carried out.) The M. L. D. is that dose which caused the death of all or a majority of animals on that dose. Variations of as much as 75% in the amount of the identical lot of barbituric acid required to produce anesthesia and death have been noted when this lot was tested at varying periods throughout a year.[21] The percentage of the M. L. D. required to produce anesthesia at these various periods, however, was not materially different. The data reported in Table V were obtained under controlled conditions so that the doses may be compared with one another, taking into consideration that the usual biological variations obtain in these experiments in which the number of animals are employed is limited.

No sedative or hypnotic effect was noted when large doses of the monosubstituted barbituric acids were injected. The replacement of a hydrogen in the β-position in one ethyl group of diethylbarbituric acid by an hydroxyl group results in the loss of the hypnotic activity. The animals did not exhibit any toxic symptoms at the doses injected.

It will be noted that diethylbarbituric acid and phenylethylbarbituric acid give a similar value for M. L. D./M. E. D. and it is this fact that has

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[20] Quade, U. S. Patent 1,461,831, prepared the calcium and magnesium diethylbarbiturate by digesting an aqueous solution of diethylbarbituric acid with calcium oxide or magnesium carbonate and concentrating the filtrate, a method quite satisfactory for the more soluble barbituric acids.

[21] These variations were probably due to differences in strains of rats, seasonal changes, etc.

TABLE V

PHARMACOLOGICAL DATA[a]

Barbituric acid derivative	No of animals	M E D., mg per kg.	M L. D , mg per kg.	% of M L D. required to abolish ear reflexes	M. L. D. / M. E D.
Diethyl	32	300	400	75	1.33
Phenyl-ethyl	24	175	240	73	1.37
n-Amyl-ethyl	18	80	210	38	2 68
Iso-amyl-ethyl	18	72	180	40	2.50
Sec.-butylcarbinylethyl	18	80	210	88	2.63
Propylmethylcarbinylethyl	18	35	90	39	2.57
Diethylcarbinyl-ethyl	16	35	90	39	2 57
Iso-propylmethylcarbinyl-ethyl	11	80	180	44	2.25
Cyclopentyl-ethyl	18	80	180	44	2.25
n-Butyl-ethyl	24	100	200	50	2.00
Isobutyl-ethyl	24	110	260	42	2.36
Sec.-butyl-ethyl	16	50	140	36	2.80
Propylmethylcarbinyl-allyl[b]	24	35	90	39	2.57
Diethylcarbinyl-allyl	27	40	100	40	2.50
Cyclopentyl-allyl	23	50	130	38	2.60
n-Butylmethylcarbinyl-ethyl	20	60	140	43	2.33
β-Hydroxyethyl-ethyl	7	Absent	> 2000		
Diethylcarbinyl	5	Absent	> 4000		
Propylmethylcarbinyl	5	Absent	> 5000		
Cyclopentyl	5	Absent	> 1000		
Sec.-butyl	5	Absent	> 1000		

[a] We are indebted to W. E. Fry for his careful and painstaking work in administering the solutions of the sodium salts and in observing the condition of the animals at regular intervals after the administration of each compound.

[b] Boedecker and Ludwig, *Arch. exp. path. Pharmakol.*, **139,** 361 (1929), mention this acid.

undoubtedly led to the many statements that the various barbituric acids are not essentially different in their action.

It is possible by varying the substituent groups to change or modify the pharmacological properties of the barbituric acids. Dimethyl and hydroxyethyl-ethylbarbituric acids are devoid of hypnotic activity, while di-iso-amylbarbituric acid causes only muscular incoördination. Propylmethylcarbinyl-ethylbarbituric acid is eight times as active as diethylbarbituric acid, and twice as active as iso-amyl-ethylbarbituric acid. n-Butylmethylcarbinyl-ethylbarbituric acid is three times as active as its isomer, di-n-butylbarbituric acid. *Sec.*-butyl-ethylbarbituric acid is twice as effective as n-butyl-ethylbarbituric acid. While three-fourths of the M. L. D. of diethyl and phenyl-ethylbarbituric acid is required to produce a state of anesthesia in rats, only two-fifths of the M. L. D. of the various amyl-ethylbarbituric acids are required. Death after the administration of a fatal dose of the amyl-ethylbarbituric acids occurs usually within the hour, while with diethylbarbituric acid it is delayed for ten to twenty-four hours. On the other hand, animals recover from a sub-lethal dose of iso-amyl-ethylbarbituric acid in half the time required for recovery from diethylbarbituric acid, indicating that the body is able to destroy or eliminate the one more readily than the other. Eddy,[22] who administered various barbituric acids orally to cats, noted that they did not act in an identical manner. Loevenhart,[23] found that iso-amyl-ethylbarbituric acid was more than five times as effective as diethylbarbituric acid in protecting rabbits against death from procaine hydrochloride.

When considered from a molecular basis, the differences are even more significant; for example, a molecule of iso-amyl-ethylbarbituric acid is five times as effective as a molecule of diethylbarbituric acid, while a molecule of propylmethylcarbinyl-ethylbarbituric acid is ten times as effective in producing anesthesia in rats.

These changes, caused by varying the substituent groups, have been observed in mice, rats and dogs. It is quite probable that in man somewhat similar relationships hold qualitatively if not quantitatively. The selection of the most suitable member of that group having the highest therapeutic index, for medical use, must be dependent on additional pharmacological factors.

In considering the isomeric amyl-alkylbarbituric acids, slight variations only are noted in the therapeutic index. It is probable that a 10% variation in this ratio may occur due to biological variations beyond the control of the investigator. Consequently one could not ascribe the differences obtained in the therapeutic index to differences in the structure of the amyl groups. With the isomeric butyl-ethylbarbituric acids the differences in the therapeutic index seem too wide to be ascribed solely to biological variation and indicate the superiority of the *sec.*-butyl group in this series. In the butyl-alkyl series, Volwiler's[3c] data show that while the *sec.*-butyl-allylbarbituric acid was effective at a lower dose than was the iso- or *n*-butyl derivative, it had the lowest ratio for M. L. D./M. E. D. This is in contrast to the butyl-ethyl series in which the *sec.*-butylethylbarbituric acid gives the highest therapeutic ratio.

The most striking effect was the observation that the *sec.*-butylethyl and both the propylmethylcarbinyl and the diethylcarbinylethyl and allylbarbituric acids were effective in half the amount required for the primary isomers. In contrast to this, isopropylmethylcarbinyl and cyclopentyl-ethylbarbituric acids were no more effective than the primary isomers, while the cyclopentyl-allyl-barbituric acid was almost as effective as the propyl-methylcarbinyl isomers. The pharmacological significance of this difference in the action of the secondary groups is being investigated.

The therapeutic indices of the *sec.*-butyl, *sec.*-amyl and *sec.*-hexyl deriva-

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[22] Eddy, *J. Pharmacol*. **33**, **43** (1928).

[23] Knoefel, Herrick and Loevenhart, *ibid.*, **33**, 265 (1928).

tives show a slight decrease as the molecular weight increases, although less of the *sec.*-amyl derivative is required to produce anesthesia than of the *sec.*-butyl or the *sec.*-hexyl derivatives.

The writers wish to express their appreciation to Dr. G. H. A. Clowes, Director of the Lilly Research Laboratories, for his suggestions.

Summary

1. The following new esters of diethylmalonate have been prepared and described: diethylcarbinyl, cyclopentyl, n-butyl-allyl, β-hydroxyethyl-ethyl, diethyl-carbinyl-ethyl, isopropylmethylcarbinyl-ethyl, cyclopentyl-ethyl, n-butylmethylcarbinyl-ethyl, di-n-propylcarbinyl-ethyl, phenyl-ethyl-ethyl and n-heptyl-ethyl.

2. The following new barbituric acids have been prepared and described: cyclopentyl, cyclopentyl-ethyl, n-butyl-methylcarbinyl-ethyl, propylmethylcarbinyl-allyl, diethylcarbinyl-allyl, and cyclopentyl-allyl barbituric acids.

3. No marked difference was found in the ratio, M. L. D./M. E. D. of the various isomeric amyl-ethyl or allyl barbituric acids. The ratio obtained for the amyl group was, however, double that obtained for diethyl or phenyl-ethylbarbituric acid. The secondary isomers usually were effective at a much lower dose than were the primary.

Indianapolis, Indiana

[Contribution from the Laboratorium fuer Chemische Technologie der Universitaet Wien, Vienna, Austria, and Northwestern University Medical School, Department of Research Bacteriology, Chicago, Illinois]

TWO ISOMERIC QUINONEDITHIOGLYCOLIC ACIDS

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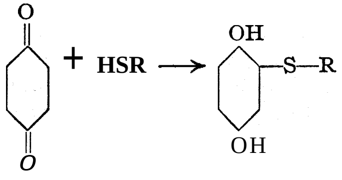
In the course of some work on the formation and properties of a variety of thioindigoid derivatives, the preparation of a 1,4-benzoquinone-2,5-dithioglycolic acid was attempted.

Usually the arylthioglycolic acids are prepared by alkaline condensation of the corresponding mercaptan with monochloro-acetic acid. As to the method of preparing the quinonedithioglycolic acids a general procedure was given by German Patent 175,070. According to this patent, p-quinones are found to react with substances represented by the general formula RSH (R representing an acid radical) as indicated by the equation



This reaction is said to proceed further when a second mole of quinone oxidizes the hydroquinone-monothioderivative to the corresponding quinone. A third and fourth RS group is said to be introduced by this method with primary formation of the corresponding hydroquinone derivatives by repeating the reaction.

The patent mentioned a variety of substances to be used as RSH. However, no reference could be found for the reaction with thioglycolic acid, which apparently is of possible value. In fact, the reaction did not proceed, as we found, in the way indicated by the general equation given, since under all circumstances tested the reaction product consisted chiefly of two isomeric 1,4-benzoquinonedithioglycolic acids, which were separated by their different solubilities in ether.

Upon treatment of the two isomers with dehydrating agents, they behave differently. The one which forms the main part of the reaction yields finally an intensely violet substance if added to an excess of chlorosulfonic acid. It dyes cotton (vat dye) as well as wool (acid dye) a greenish-blue color. The fact that condensation actually occurred makes it most likely that the isomer in question is the 1,4-benzoquinone-2,5-dithioglycolic acid (2,6-substitution is unlikely but possible).

The second isomer upon treatment in the above manner yielded no colored substance. Its structure therefore is given as the 1,4-benzoquinone-2,3-dithioglycolic acid.

The dual behavior of the thioindigoid dye prepared from the 2,5-isomer as noted above possibly gives a clue as to the structure of the dye obtained, even though it was not obtained in a sufficient degree of purity to insure reliable analysis. It will be discussed elsewhere.

The 1,4-benzoquinone-2,5-(2,6?)-dithioglycolic acid was found to exist in two modifications: brown needles (from ether by precipitation with ligroin below 30–40°) and a red powder m. p. 171 (from other solvents at elevated temperatures). The two modifications can be converted into each other and crystallized from water in deep violet, sometimes nearly black, needles containing one mole of water; the water of crystallization is lost at 50–60° with formation of the intensely red colored modification mentioned above.

Experiments

Preparation and Behavior of the **Two** Isomeric **1,4-Benzoquinone-dithioglycolic** Acids.[1]—After a number of preliminary experiments varying the relative amounts of the components, temperature of the reaction and solvents to be used, the following procedure was finally adopted for the preparation and isolation of the two isomeric quinone dithioglycolic acids. Ten grams of quinone were dissolved in 100 cc. of chloroform and 8.6 g. of thioglycolic acid dissolved in 100 cc. of chloroform was added. The reaction mixture first turned greenish-black (quinhydrone) but began to deposit a red precipitate

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[1] The preliminary experiments were carried out with H. A. Beatty.

after thirty-six hours. After seventy hours the mixture was filtered and dried in a vacuum. Upon extraction with ether for twenty-four hours in a Soxhlet apparatus, a red residue was left. This residue was then extracted with benzene several times to insure its freedom from hydroquinone and repeatedly recrystallized from water. Finally violet (black) needles were obtained melting at 205" (const.). The figures obtained by the analysis correspond well with the values for a I,4-benzoquinonedithioglycolic acid.

Anal. Subs., 5 205 mg.: CO_2, 7.904 mg.; H_2O, 1.461 mg. Subs., 0.1016: $BaSO_4$, 0.1697. Calcd. for $C_{10}H_8O_6S_2$: C, 41.04; H, 2.80, S, 22 26. Found: C, 41.42; H, 3.14; S, 21.59.

The ether extract was evaporated to dryness and extracted with benzene in a Soxhlet apparatus. The extraction was stopped when all of the hydroquinone present was dissolved. The residue finally gave, on repeated recrystallization from water, violet (black) needles which melted at 171° and analyzed well for 1,4-benzoquinonedithioglycolic acid plus one mole of water.

Anal. Subs., 5.181 mg.: CO_2, 7.591 mg.; H_2O, 1.578 mg Calcd. for $C_{10}H_8O_6S_2 \cdot H_2O$: C, 39.19; H, 3.29. Found: C, 39.96; H, 3.41.

The water of crystallization is lost at about 60° with the formation of a bright red substance. Its formation is also noticeable when the melting point is determined. These red needles analyze well for a water-free quinonedithioglycolic acid.

Anal. Subs., 5.301 mg.: CO_2, 8.066 mg.; H_2O, 1.606 mg. Calcd. for $C_{10}H_8O_6S_2$: C, 41.66; H, 2.80. Found: C, 41.50; H, 3.39. Subs., 0.0155: after drying in a vacuum of 13 mm. to constant weight, 0.0145; diff , 0.0010. Calcd. for $C_{10}H_8O_6S_2 \cdot H_2O$: H_2O, 5.89. Found: H_2O, 6 45.

Upon the recrystallization from water of both isomers an appreciable amount of substance is lost, the mother liquors become brown and contain decomposition products of the original acid. These mother liquors, upon acidification, dye wool a clear and fast brown color; the substances found have not been investigated.

The hydrated and water-free modifications are interconvertible. Both forms dissolve in ether giving an orange-red solution and are precipitated from such solutions in the form of brown needles by an excess of ligroin. These needles apparently represent a second water-free modification (containing no solvent of crystallization). It is stable only at low temperatures, since it was found that when the ligroin precipitation is carried out at 40° the red modification is obtained immediately. The brown modification upon recrystallization from water also yields the violet (black) needles containing one mole of water.

The two isomeric quinonedithioglycolicacids described are the main products of the reaction. There are, however, other substances formed and found in the various extracts and mother liquors. Their isolation has not yet been attempted due to the comparatively small amounts formed.

The 1,4-benzoquinonedithioglycolic acid, m. p. 205°, was treated in the usual manner with chlorosulfonic acid but was found not to condense. The acid, therefore. is most likely the 1,4-benzoquinone-2,3-dithioglycolic acid

The second isomer, m. p. 171°, condensed readily upon heating with an excess of chlorosulfonic acid for twelve hours at 50–70°. The thioindigoid dye was isolated. This isomer therefore represents a 1,4-benzoquinone-2,5(2,6?)-dithioglycolic acid.

Summary

Two isomeric benzoquinonedithioglycolic acids have been prepared. Their structures are given and their properties described. Upon condensa-

tion with chlorosulfonic acid the 1,4-benzoquinone-2,5-(2,6?)-dithioglycolic acid forms a thioindigoid dye.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE EFFECT OF DISSOCIATED WATER VAPOR ON CERTAIN VEGETABLE OILS

BY G. I. LAVIN AND E. EMMET REID

RECEIVED FEBRUARY 15, 1930 PUBLISHED JUNE 6, 1930

Introduction

Bonhoeffer[1] has shown that atomic hydrogen will attack the double bond in a straight-chain compound like oleic acid. Watermann and Bertram[2] found that active hydrogen (dried) caused the oleic acid to undergo a polymerization along with the hydrogenation. Wood[3] has conducted some experiments with cottonseed oil and atomic hydrogen and obtained a white solid. In a recent paper Urey and Lavin[4] have shown that water vapor dissociated in a discharge tube is an energetic reducing agent and it is the purpose of this note to describe some experiments carried out with dissociated water vapor and cottonseed oil.

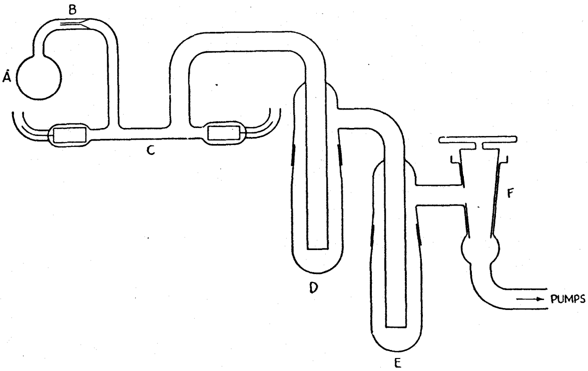

Fig. 1.—Apparatus for treatment of oils with dissociated water vapor.

Apparatus.—The apparatus used is shown in the accompanying diagram. It consists essentially of a source of water vapor A, a capillary B, discharge tube C and traps E and F.

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[1] Bonhoeffer, *Z. physik Chem.*, *113*, **199 (1924).**

[2] Watermann and Bertram, *Chem. Umschau Fette, Oele, Wachseu. Harze, 34*, *255* **(1927).**

[3] Private communication.

[4] Urey and Lavin, THIS JOURNAL, 51, **3290 (1929).**

Experimental

The cottonseed oil was poured into the first trap E, so that it formed a film on the walls; the second trap F was cooled with dry ice and ether to protect the pumps from water vapor. Under the influence of the active gas from the discharge the oil was almost immediately converted into a solid.

The reaction takes place rapidly and appears to go best on the walls; the product forms as a tightly stretched film or skin. A small piece of iron was placed in the bulk of the oil and by the use of an electromagnet it was possible to stir the mass and so renew the oil surface. With this arrangement it was easy to observe the continued formation of the film.

The product is a white solid, fibrous and resilient. It is insoluble in water and in all of the organic solvents tried and can be washed free of unchanged oil by ether. When the solid is shaken with ether it seems to absorb the ether and swells somewhat. The substance does not melt but chars. Under the same conditions olive oil, linseed oil and castor oil yield white, insoluble substances which have similar properties.

Summary

It has been shown that cottonseed oil is attacked by the active gas from a water vapor discharge tube. Fibrous substances are produced which are insoluble in ether and other organic solvents. Olive oil, linseed oil and castor oil yield similar compounds.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE ACTION OF THE SYSTEM $Mg + MgBr_2$ UPON TRIPHENYLCARBINOL, TRIPHENYLBROMOMETHANE AND UPON TRIPHENYLMETHYL[1]

BY M. GOMBERG AND W. E. BACHMANN

RECEIVED FEBRUARY 17, 1930 PUBLISHED JUNE 6, 1930

The method used by Conant[2] for the reduction of carbinols directly to free radicals suggested that a similar reduction, but in non-aqueous solvents, might be accomplished by the system $Mg + MgBr_2$.[3] Triphenylmethyl was actually produced in this manner from triphenylcarbinol, but its formation, we found, was brought about by a secondary reaction, and not by direct reduction of the carbinol.

When a solution of triphenylcarbinol in a mixture of ether and benzene

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[1] From a paper presented before the Division of Organic Chemistry, American Chemical Society, at the third Organic Symposium, Princeton, New Jersey, December 9, 1929.

[2] Conant, THIS JOURNAL, 45, 2466 (1923).

[3] From experiments by Dr. F. J. Van Natta, this Laboratory.

is heated with magnesium bromide alone, the basic salt, $MgBr(OH)\cdot(C_2H_5)_2O$, precipitates from the solution, and the reaction proceeds to the extent of 75–80%, as follows

$$(C_6H_5)_3COH + MgBr_2 \longrightarrow (C_6H_5)_3CBr + MgBr(OH) \qquad (1)$$

When, however, the carbinol is heated with a mixture of $MgBr_2 + Mg$, and the reaction product is treated with water in absence of air, there results a mixture, in varying proportions, of triphenylmethyl and triphenylmethane. The former was interpreted as originating from the action of metallic magnesium on carbinol bromide (Equation 2), and the methane as coming from some triphenylmethylmagnesium bromide (Equation 3); triphenylchloromethane is well known to give an analogous Grignard reagent.

$$2(C_6H_5)_3CBr + Mg \longrightarrow 2(C_6H_5)_3C + MgBr_2 \qquad (2)$$

$$(C_6H_5)_3CBr \xrightarrow{Mg} (C_6H_5)_3CMgBr \xrightarrow{HOH} (C_6H_5)_3CH + MgBr(OH) \qquad (3)$$

Our erstwhile interpretation that Reactions 2 and 3 are merely competing reactions became untenable when it was found that the longer the reaction mixture (carbinol + Mg + $MgBr_2$) is heated, the less triphenylmethyl and the more triphenylmethane (i. e., Grignard reagent) is obtainable. Instead of competing, the triphenylmethyl represents, it seemed, an intermediate stage in the formation of the final magnesium compound

$$(C_6H_5)_3CBr \xrightarrow{Mg} (C_6H_5)_3C \xrightarrow[MgBr_2]{Mg} (C_6H_5)_3CMgBr \qquad (4)$$

In order to test this conclusion we studied in detail the reaction between triphenylbromomethane and magnesium.

One gram-mole of the carbinol bromide was found to react with one gram-atom of magnesium, and the Grignard reagent is produced in practically quantitative yield. However, when only one-half that amount of metal is used, no Grignard reagent is present at the end of the reaction and the solution contains only triphenylmethyl and magnesium bromide, as may be represented by Equation 2, although the mechanism may, in reality, be more complex than indicated (see page 2459). If an additional one-half gram-atom of magnesium is now added at this stage, the triphenylmethyl is completely converted into triphenylmethylmagnesium bromide. Obviously, the second part of the process must consist in the reaction

$$2(C_6H_5)_3C + MgBr_2 + Mg = 2(C_6H_5)_3CMgBr \qquad (5)$$

This inference has been verified by experiment. Pure triphenylmethyl has been found to react with the binary system quantitatively in accordance with Equation 5.

The failure to recognize that triphenylmethyl is an intermediate *stage* in the production of triphenylmethylmagnesium halide has been the cause of the many perplexing contradictions in the discussion on this subject by Schmidlin and Chichibabin.[4]

That free radicals with a transitory existence play an important role in the mechanism whereby a Grignard reagent is formed has been previously suggested by us:[5] (a) MgX_2 (activator) + Mg $2MgX$, or in absence of activator, $RX + Mg = R + MgX$; (b) $RX + MgX = R + MgX_2$; (c) $R + R = RR$; (d) $R + MgX = RMgX$, (c) and (d) being two competing reactions. Recently Kinney[6] and Gilman and co-workers[7] have interpreted the formation of the Grignard reagent substantially in accordance with our hypothesis. The latter investigators also remark that "it is possible to prepare triphenylmethylmagnesium iodide from triphenylmethyl and magnesious iodide,"[8] but no experimental details are given.

The results here presented constitute a realization of our surmise—*a Grignard reagent can be produced from a free radical and the system* $MgX_2 + Mg$.

Experimental

Triphenylmethylmagnesium Bromide

Schmidlin, who first prepared triphenylmethylmagnesium chloride, found it necessary to use iodine as an activator and to heat the mixture of the reactants for several hours or, otherwise, instead of the normal "&modification," there was produced much of the "a-modification," presumably a quinonoid isomer. This so-called or-modification, in our opinion, is largely the ether complex of triphenylmethyl.

We now find that the carbinol bromide reacts far more readily than the chloride. No activator is needed, the reaction proceeds at room temperature, and more rapidly on gentle warming. The triphenylmethylmagnesium bromide is only slightly soluble in ether, but is soluble in a mixture of one part of ether and two parts of benzene, and we used largely such a mixture. For more rapid reaction, magnesium powder or ribbon was employed, but for study of the rate of reaction we used magnesium rods, about 1.5 X 0.7 cm.; the rods could be quickly removed from the solutions in large test-tubes, weighed and replaced for continuation of the experiment. **A** number of experiments were carried out, varying the amount of magnesium used and varying the time allowed for the reaction from a few minutes to over a year. It was definitely established that not more than a gram-atom of magnesium enters into the reaction under any conditions (Equation 3).

Triphenylbromomethane, 16.2 g., and 1.34 g. of magnesium ribbon (calcd. 1.22 g.) in a mixture of 25 cc. of ether and 50 cc. of benzene were heated on a steam-bath. The

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[4] Schmidlin, *Ber.*, **39,** 628, 4183 (1906); **40,** 2316 (1907); **41,** 423, 430 (1908) Chichibabin, ibid., **40,** 3965 (1907); **42,** 3469 (1909).

[5] Gomberg and Bachmann, THIS JOURNAL, 49, 256 (1927).

[6] C. R. Kinney, in a paper before the Division of Organic Chemistry of the American Chemical Society at the meeting in Minneapolis, Minnesota, September, 1929.

[7] Gilman and Fothergill, THIS JOURNAL, 50, 3334 (1928); Gilman and Kirby, *ibid.*, 51,1572 (1929).

[8] Gilman and Fothergill, *ibid*, 51, 3152 (1929). The same information, in the same terms, was communicated in a letter to one of us (G) in February, 1929, when the results described in this paper had been already well established in this Laboratory.

solution was protected against access of air and against light in order to prevent decomposition of the triphenylmethyl. The reaction was apparently completed in less than one hour. The clear solution was filtered from the slight excess of magnesium through a sintered glass funnel and hydrolyzed, all in an atmosphere of nitrogen. The loss in weight of the magnesium was 1.20 g. The $Mg(OH)_2$ in the hydrolyzed mixture required for neutralization 48.7 cc. of N H_2SO_4, calcd. 50.0 cc. The crude triphenylmethane, obtained on evaporation of the ether–benzene solution, was recrystallized from benzene; weight 15.66 g., which is equivalent to 11.74 g. of benzene-free triphenylmethane. The quantity of the latter, the amount of $Mg(OH)_2$ and the weight of metallic magnesium that had dissolved show that the yield of the Grignard reagent was 96–97%.

In another experiment, the triphenylmethylmagnesium bromide was carbonated and the yield of triphenylacetic acid was practically quantitative.

Triphenylmethylmagnesium bromide and iodide can be readily prepared from the chloride. An equivalent amount of the corresponding magnesium halide is added to the solution of the carbinol chloride, whereupon magnesium chloride precipitates. The latter does not interfere with the subsequent course of the reaction. Activation by means of iodine, when the carbinol chloride is employed, is undoubtedly equivalent to adding magnesium iodide.

Isolation of the Grignard Reagent.—When to a concentrated solution of triphenylmethylmagnesium bromide in benzene–ether a further amount of ether is added, the etherate of the Grignard reagent comes down as granular crystals. For purposes of analysis it was prepared as follows. A rod of magnesium was allowed to react at room temperature with a solution of 8 g. of triphenylbromomethane in 75 cc. of ether–benzene (2 :) After one day the rod was coated with a deposit of large colorless transparent prisms. When a sufficiently large crop of these crystals had collected, they were detached from the rod, freed from some triphenylmethyl by washing with ether, and dried in a current of nitrogen. For analysis, a sample was hydrolyzed and the resulting products—triphenylmethane, $Mg(OH)_2$ and bromo ion were determined.

Anal. Subs., 1.592 g. Calcd. for $(C_6H_5)_3CMgBr \cdot 2(C_2H_5)_2O$: $(C_6H_5)_3C$, 49.1; Mg, 4.9; Br, 16.1. Found: $(C_6H_5)_3C$, 48.7; Mg, 4.9; Br, 16.2.

Triphenylmethyl from Triphenylbromomethane and Magnesium

Triphenylbromomethane (1 Mole) + Mg (0.5 Atom).—A mixture of 16.2 g. of triphenylbromomethane and 0.6 g. of magnesium ribbon in 25 cc. of ether and 50 cc. of benzene was heated on the steam-bath. In half an hour all the magnesium disappeared. No magnesium hydroxide was produced when the mixture was hydrolyzed; consequently, no Grignard reagent had been present. Air was passed into the ether–benzene solution, and 10.4 g. of pure triphenylmethyl peroxide was obtained, which, assuming an 80% yield, corresponds to about 12.2 g. of triphenylmethyl, calcd. 12.15. No triphenylmethane was found in the filtrate from the peroxide.

We have represented the formation of triphenylmethyl by Equation 2. Actually, the mechanism may be more complex. Indeed, Schmidlin has shown that triphenylmethylmagnesium chloride can enter into reaction with triphenylchloromethane, giving rise to triphenylmethyl, and he ascribed to this reaction the presence of any triphenylmethyl in admixture with his preparations of the Grignard reagent

$$(C_6H_5)_3CMgX + (C_6H_5)_3CX = 2(C_6H_5)_3C + MgX_2 \qquad (6)$$

With our reagents we find that this reaction proceeds rapidly and completely. When to a solution of triphenylmethylmagnesium bromide an equivalent amount of triphenylbromomethane is added and the mixture is warmed for a few minutes, triphenylmethyl results in quantitative yield.

In view of the rapidity of Reaction 6, it seems quite likely that triphenylmethyl is produced not as represented in Equation 2 but by inter-reaction of Grignard reagent, initially formed, and unchanged triphenylbromomethane, *i. e.*, in two successive steps represented by the equations (3) and (6), respectively.

Triphenylmethyl + Mg + $MgBr_2$ (or MgI_2)

A number of experiments were performed on solutions of the free radical which had been prepared either according to Equation 6 or from triphenylchloromethane by means of silver or zinc. The results were quite satisfactory, but in order to make certain that our solutions of the radical were entirely free from any possible admixture of carbinol halide, the work was repeated with pure triphenylmethyl that had been recrystallized from acetone.

To a solution of 14.3 g. of triphenylmethyl in 60 cc. of benzene was added a solution of 9 g. of anhydrous magnesium bromide (prepared from $HgBr_2$ + Mg)[9] in 40 cc. of benzene and 60 cc. of ether. A small quantity of crystals precipitated, presumably a molecular compound of triphenylmethyl and $MgBr_2$. A coil of magnesium ribbon was introduced into the solution, and the mixture was gently heated on the steam-bath in an atmosphere of nitrogen; the upper end of the reflux condenser was connected to a mercury trap. The reaction started immediately and the mixture was heated for three hours. According to Equation 5, 0.71 g. of metallic magnesium should have reacted; found, 0.66 g., or 93% of the calculated value. The filtered solution was decomposed with water. The magnesium hydroxide so produced required 56.8 cc. of N H_2SO_4, calcd. 58.4 cc., and there were obtained 13.7 g. of pure triphenylmethane and 0.7 g. of triphenylmethyl peroxide.

In another experiment 9.0 g. of triphenylmethyl dissolved 0.445 g. of Mg (calcd. 0.450), and there was obtained on hydrolysis of the reaction product 7.9 g. of triphenylmethane.

Isolation and Analysis of the Triphenylmethylmagnesium Bromide.—Thirteen grams of crystalline triphenylmethyl was added to a solution of 9 g. of $MgBr_2$ in 120 cc. of ether–benzene (2:1), and the solution was heated for several hours with somewhat more than the required amount of magnesium ribbon. To the filtered solution was added a single crystal of triphenylmethylmagnesium bromide (obtained from triphenylbromomethane + magnesium), when sudden crystallization took place and in a short time the solution was half-filled with glistening prisms. The crystals were filtered, washed repeatedly with pure ether, and dried in a stream of nitrogen. The compound was found to be identical with the triphenylmethylmagnesium bromide obtained directly from triphenylbromomethane.

Anal. Subs., 14.56 g. Calcd. for $(C_6H_5)_3CMgBr\cdot 2(C_2H_5)_2O$: $(C_6H_5)_3C$, 49.1; Mg, 4.9; Br, 16.1. Found: $(C_6H_5)_3C$, 49.2; Mg, 4.7; Br, 16.1.

Triphenylmethyl + Mg + $MgBr_2$ at Room Temperature.—Ten and three-tenths grams of triphenylmethyl was added to a solution of 4.6 g. of $MgBr_2$ in 120 cc. of ether–benzene (1:2), containing 0.67 g. of magnesium ribbon. In one week at room temperature there was dissolved 0.50 g. of magnesium, and there was produced a 97% yield of triphenylmethylmagnesium bromide.

Triphenylmethyl + Mg + MgI_2.—A mixture of 12.2 g. of triphenylmethyl, 11 g. of magnesium iodide and 2.5 g. of magnesium ribbon in 150 cc. of ether-benzene (1:2) was heated on the steam-bath for several hours. The magnesium loss was 0.61 g., calcd., 0.608. Hydrolysis of the reaction product yielded 11 g. of triphenylmethane.

Reaction with Carbon Dioxide.—A solution of triphenylmethylmagnesium iodide was prepared from 12 2 g. of triphenylmethyl. A stream of dry carbon dioxide was

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[9] Gomberg and Bachmann, THIS JOURNAL, 49,2586 (1927).

passed into this solution for three hours; during this time a large amount of light yellow precipitate appeared. Decomposition with dilute acid gave a product from which 12 g. of pure triphenylacetic acid was obtained.

Relative Proportions of $(C_6H_5)_3C$ and $(C_6H_5)_3CMgBr$

It is now obvious that in the process of "grignarding" triphenylbromomethane, no Grignard reagent is present until after one-half of the entire amount of magnesium has reacted. After the half-way mark, generation of Grignard reagent can come about only as a consequence of the reaction between triphenylmethyl and the system Mg + $MgBr_2$. This reaction proceeds to completion in virtue of the fact that Step c (p. 2457) is, in this case, reversible: R + R RR. The relative quantities of free radical and of triphenylmethylmagnesium bromide that are present at any time during the reaction may be expressed graphically as in Fig. 1.

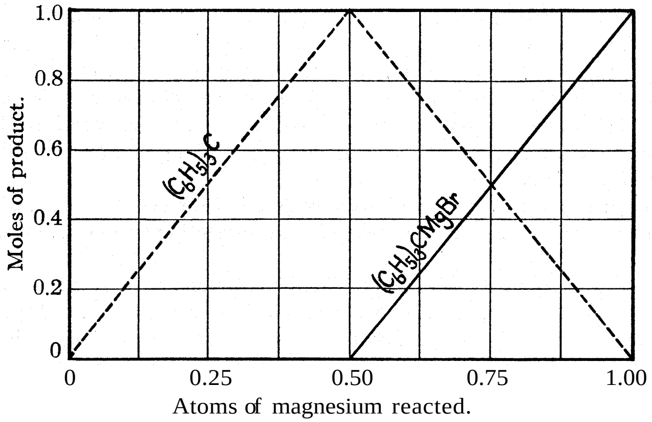

Fig. 1.—Amounts of triphenylmethyl and Grignard reagent in the reaction between triphenylbromomethane and magnesium.

Experiments conducted at room temperature and interrupted before a whole gram-atom of magnesium had reacted gave results which are in accordance with the curves. The following special experiment gave the two components in the ratio as anticipated, 50% each.

Triphenylbromomethane (1 Mole) + Mg (0.75 Atom).—Triphenylbromomethane, 16.2 g., and 0.912 g. of magnesium ribbon were heated together in 75 cc. of ether–benzene. In less than an hour all of the metal disappeared. The magnesium hydroxide produced on hydrolysis required 25.0 cc. of N H_2SO_4 for neutralization. This corresponds to a 50% yield of $(C_6H_5)_3CMgBr$ (see Fig. 1). From the benzene solution, after passing air into it, there were obtained 5.88 g. of triphenylmethyl peroxide (**calcd.** 6.5) and 6.0 g. of triphenylmethane (calcd. 6.1).

Summary

It has been shown that triphenylcarbinol reacts in anhydrous solvents **with** magnesium bromide and forms triphenylbromomethane.

Triphenylbromomethane reacts with metallic magnesium far more readily than the chloride, and gives rise to triphenylmethylmagnesium bromide. This has been isolated in crystalline state and analyzed.

The formation of triphenylmethylmagnesium bromide takes place in two successive stages: (a) formation of triphenylmethyl; (b) formation, from that, of the magnesium compound, $2\ R_3C + Mg + MgX_2 = 2\ R_3CMgX$. The formation of the triphenylmethyl is in itself most probably the result of two successive reactions: $R_3CX + Mg = R_3CMgX$; $R_3CMgX + R_3CX = 2\ R_3C + MgX_2$.

The formation of triphenylmethylmagnesium halide from triphenylmethyl and the system $Mg + MgX_2$ lends much support to the hypothesis that the action of the binary system is through the intermediate formation of the active compound MgX.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

TOXICAROL. A CONSTITUENT OF THE SOUTH AMERICAN FISH POISON CRACCA (TEPHROSIA) TOXICARIA[1]

BY E. P. CLARK

RECEIVED FEBRUARY 17, 1930 PUBLISHED JUNE 6, 1930

In connection with a survey of fish poisoning plants as sources of insecticides now in progress in this Laboratory, a chemical examination of the roots of Cracca (*Tephrosia*) *toxicaria* was made.[2] It was shown that this plant material contains a crystalline substance which in high dilutions is toxic to fish. The crude crystals had a greenish-yellow color and a melting point of 200–203°. Closer examination revealed that the material was composed of at least two substances. The one that occurs in much the greater proportion is a bright canary yellow, optically inactive compound which has a melting point of 219° (corr.). It has the molecular formula $C_{23}H_{22}O_7$ and has one hydroxyl and two methoxyl groups. The name toxicarol has been assigned to it.

The second substance is a pale green crystalline compound which is separated from toxicarol only with difficulty. Owing to the small quantity of the plant available it was impossible to obtain sufficient crystalline material to carry the fractionation of the second substance to a state of certain analytical purity. Its optical properties, however, were readily determined, and from these data it was shown that the substance was identical with an optically inactive dimethoxy compound having the formula $C_{23}H_{22}O_6$ which is found in *Derris* and *Cube* roots.

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[1] The name *Tephrosia* Pers. is antedated by *Cracca* and under the American code of Botanical Nomenclature all species of *Tephrosia* should bear the generic name *Cracca*.

[2] The material was received from the Department of Agriculture, Georgetown, British Guiana, through the American Vice Consul, Harold R. Brown.

It is of interest to note that the molecular formula for toxicarol differs from the formula of rotenone by one oxygen atom only, whereas the formula for the second compound is identical with that of rotenone. Furthermore, both substances have two methoxyl groups, as does rotenone, and both are approximately as toxic to fish. These considerations, together with the fact that all three substances are found in *Derris,* indicate that possibly some common structural relationships exist among the three bodies. Further work, now in progress, is expected to throw more light upon this matter.

Experimental

Fifty grams of the ground roots of *Cracca toxicaria* were completely exhausted with ether. The resulting extract, after the removal of the solvent, was dissolved in 30 cc. of hot methanol and then made alkaline with 10 cc. of an aqueous 5% sodium hydroxide solution. The mixture was immediately heated to its boiling point, causing a tarry substance to separate. The supernatant liquid was decanted, diluted with three volumes of water, made acid to congo red with sulfuric acid and extracted with chloroform. The chloroform extract was washed with water, dried with sodium sulfate, filtered and evaporated to a small volume. Several volumes of methanol were then added to the concentrate and the solution was evaporated to a volume of approximately 10 cc. Upon allowing the liquid to cool, crystallization began at once. The yield was 0.65 g. or 1.3% of the drug taken. As stated before, the product had a greenish-yellow color and a melting point of 200–203°.

Pure toxicarol was obtained from this material by dissolving the crude crystals in hot chloroform, filtering the solution through norite, again heating the solution to its boiling point and then adding about 12 volumes of boiling alcohol. The solution was maintained in a state of vigorous boiling until it became practically free from chloroform, at which time toxicarol began to crystallize. The process was soon completed, and the crystals were filtered from the boiling liquid. The product thus obtained had a melting point of about 215". Two or three recrystallizations of this material by the method just given resulted in a product having a constant melting point of 219° (corr.). It consists of bright, greenish-yellow, six-sided plates and rods whose refractive indices are: n_α, 1.580 (frequent); n_β, 1.618 (common); and n_γ, >1.768, all ±0.003. In parallel polarized light with crossed nicols the extinction is inclined and the elongation is negative. Double refraction is very strong. Many of the plates are so thin that only first order white and yellow colors are shown. Frequently plates remain bright in all positions when the stage is rotated. In convergent polarized light with crossed nicols the large plates show distinct biaxial interference figures with a large axial angle. The optic sign is positive.[3]

Anal. Calcd. for $C_{23}H_{22}O_7$: C, 67.30; H, 5.41; CH_3O (2), 15.1. Found: C, 67.09; H, 5.41; CH_3O, 15.3.

Toxicarol Benzoate.—Two cc. of benzoyl chloride was added to a solution of 2 g. of toxicarol in 20 cc. of hot pyridine. After an hour the reaction mixture was poured into 300 cc. of water, causing the separation of an oil. This was removed from the mother liquor by decantation and dissolved in 75 cc. of boiling alcohol. Upon cooling, 1.5 g. of toxicarol benzoate, having a melting point of 200°, separated. This was recrystallized

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[3] The optical data recorded in this communication were determined by George L. Keenan of the Food, Drug and Insecticide Administration of the U. S. Department of Agriculture. Appreciation is acknowledged for this valuable cooperation.

from its solution in chloroform by the addition of 5 volumes of methanol. It separated in rosets of fine colorless needles whose melting point was 202° (corr.). The yield was 1.35 g. Its refractive indices are n_α, 1.590; n_β, indeterminate; n_γ, 1.702. An intermediate value n,, 1.650, is also common. In parallel polarized light with crossed nicols the extinction is inclined and the sign of elongation is positive.

Anal. Calcd. for $C_{30}H_{26}O_8$: C, 70.01; H, 5.10; CH_3O (2), 12.06. Found: C, 69 68; H, 5.05; CH_3O, 12.28.

The Second Compound, $C_{23}H_{22}O_6$.—The mother liquors from the first purification of toxicarol were evaporated to dryness in vacuo, and the residue was dissolved in about 25 cc. of boiling alcohol and filtered. The filtrate. upon cooling, deposited a small crop of crystals having a light greenish-yellow color and a melting point of about 180°. Upon repeated fractional crystallization the melting point of the substance was reduced to 173°, and its color became much lighter, but there was insufficient material to resolve the substance to a state of certain analytical purity. Its crystallographic properties, however, were readily determined to be as follows. The compound crystallized in rods, many of them six-sided in outline. Their refractive indices are n,, 1.570; n_β, 1.590 (common); and $n_\gamma > 1.739$, all ±0.003. The extinction is inclined, and the elongation is negative. Most of the crystals do not extinguish sharply when examined in parallel polarized light with crossed nicols.

These properties are the same as those possessed by a substance obtained from *Derris* and *Cube* roots. This material will be reported upon shortly, when it will be shown to be an optically inactive dimethoxy compound $C_{23}H_{22}O_6$, whose melting point is 171°. A mixture of this compound and the second substance obtained from *Cracca toxicaria* melted at 172°. This and the fact that the two substances have the same optical properties prove that they are identical.

The two substances from *Cracca toxicaria* have been shown to be decidedly toxic to fish. For example, at a dilution of 1–20,000,000 at 27°, goldfish weighing approximately 2 g. were killed by toxicarol in four and one-half hours and by the $C_{23}H_{22}O_6$ compound in three hours, while rotenone given for comparative purposes, was effective in two and one-fourth hours. These toxicological data, determined by W. A. Gersdorff of the Insecticide Division of the Bureau of Chemistry and Soils, were taken from a series of experiments which will be reported in detail elsewhere. They are recorded at this time, however, to show the relative toxicity of the substances under consideration.

Summary

1. Two active fish poisons have been isolated from the roots of *Cracca toxicaria.*

2. One of these, toxicarol, predominates. It is an optically inactive compound, $C_{23}H_{22}O_7$, possessing one hydroxyl and two methoxyl groups.

3. The second substance is an optically inactive dimethoxy compound having the molecular formula $C_{23}H_{22}O_6$.

4. It has been indicated that both substances occur in *Derris* while the $C_{23}H_{22}O_6$ compound has been found also in *Cube* roots.

5. Toxicarol kills goldfish in a dilution of 1–20,000,000 at 27° in four and one-half hours. The $C_{23}H_{22}O_6$ compound at the same dilution and temperature is lethal in three hours.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE FIFTH PENTA-ACETATE OF GALACTOSE, ITS ALCOHOLATE AND ALDEHYDROL

BY M. L. WOLFROM

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In the work herein reported, the methods employed in the synthesis of the crystalline free aldehyde form of glucose[1] have been extended to galactose, and we have obtained this form of galactose penta-acetate and also its crystalline hydrate and ethyl alcoholate. This penta-acetate is of particular interest because it adds a fifth isomer to the series of four already known. Erwig and Koenigs[2] prepared the first form, m. p. 142°, of galactose penta-acetate. This beta ring form was isomerized to the alpha form of the same ring structure by Hudson and Parker[3] on heating with acetic anhydride and zinc chloride. Hudson[4] then reported a third form found in small yield in the acetylation mother liquors from the preparation of the first form. This was prepared in larger quantity by Hudson and Johnson[5] and isomerized to the fourth form by the acetic anhydride and zinc chloride reaction. These four forms were found by Hudson to conform in rotation to two alpha and beta pairs of two different ring structures and constituted the first proof, based on the isolation of crystalline derivatives, that a sugar could exist in more than one lactal or ring structure. The third form of galactose penta-acetate has been prepared in higher yield by a method recently reported by Schlubach and Prochownick.[6] The properties of the five forms of galactose penta-acetate are shown in Table I.

TABLE I

PROPERTIES OF THE FIVE PENTA-ACETATES OF GALACTOSE

Form	M. p., °C.	$[\alpha]_D$ $CHCl_3$,[a] U. S. P.
First galactose penta-acetate, β-form	142	+ 23.0
Second galactose penta-acetate, a-form	96	+107.0
Third galactose penta-acetate, β-form	98	− 42.0
Fourth galactose penta-acetate, a-form	87	+ 61.0
Fifth galactose penta-acetate, μ-form	121	− 25 (Initial)

[a] The first four forms were measured at 20°, the fifth at 26°.

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[1] M. L. Wolfrom, THIS JOURNAL, 51, 2188 (1929).

[2] E. Erwig and W. Koenigs, Ber., 22, 2207 (1889).

[3] C. S. Hudson and H. O. Parker, THIS JOURNAL, 37, 1589 (1915).

[4] C. S. Hudson, *ibid.*, 37, 1591 (1915).

[5] C. S. Hudson and J. M. Johnson, *ibid.*, 38, 1223 (1916).

[6] H. H. Schlubach and Vilma Prochownick, Ber., 62, 1502 (1929).

We have suggested[1] the name μ-glucose penta-acetate for the free aldehyde sugar acetates. This is convenient in briefly distinguishing from the a- and β-forms, as in Table I, but it has the disadvantage of not being a very rational prefix. We believe that the prefix aldehydo overcomes this difficulty and we will accordingly designate the fifth penta-acetate of galactose as aldehydo galactose penta-acetate.

Aldehydo galactose penta-acetate very readily combines with one molecule of ethyl alcohol and of water to form compounds that we do not believe are in the nature of ordinary addition compounds. Both compounds are stable to calcium chloride desiccation and it was found that the alcohol could not be removed from the alcoholate by heating at various temperatures under highly reduced pressure without decomposition of the acetate. As regards the hydrate, it need only be pointed out that the ordinary forms of sugar acetates show no tendency at all toward hydrate formation. We accordingly believe that these compounds are similar to the corresponding ones of chloral and it is interesting to note that their melting points fall in the same order, as is shown in Table II. It has been well established that these compounds of chloral are not ordinary addition compounds.

TABLE II

COMPARISON OP THE MELTING POINTS OP CHLORAL AND ITS HYDRATE AND ALCOHOLATE WITH THOSE OF ALDEHYDO GALACTOSE PENTA-ACETATE

	Chloral[a]	Aldehydo galactose penta-acetate
Ethyl alcoholate, m. p., °C.	55	133
Hydrate, m. p., °C.	47.4	125
Free form, m. p., °C.	–57.5	121

[a] J. C. Olsen, "Chemical Annual," D. Van Nostrand, Co., Inc., New York, 1926, 6th ed.

If these two compounds of aldehydo galactose penta-acetate are not ordinary addition compounds, then they must be the aldehydrol and the ethyl-hemi-acetal. Galactose aldehydrol has been postulated by Lowry and Smith[7] as an intermediate in mutarotation and an analysis of data has led these authors to conclude that this form exists at equilibrium to the extent of 12% of the sugar present. Levene and Meyer[8] prepared the liquid aldehydo pentamethylgalactose, and by using methyl alcohol containing hydrogen chloride, were able to obtain the dimethyl acetal (b. p., 118–120°, 0.6 mm.).

The alcoholate and hydrate of aldehydo galactose penta-acetate show rotation changes in U. S. P. chloroform solution that are probably due to dissociation of the alcohol and water, respectively. These are plotted in Fig. 1 and Pig. 2 and both curves exhibit a distinct break in the early

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[7] T. M. Lowry and G. F. Smith, J. Phys. *Chem.*, 33, 9 (1929).

[8] P. A. Levene and G. M. Meyer, J. *Biol. Chem.,* 74,695 (1927).

course of the change. The free form shows a continuous change of rotation in chloroform. That this change is due to combination with the ethyl alcohol in the U. S. P. chloroform used is made probable by the fact that the rotation of this form was constant in pure acetylene tetrachloride solution. The final rotation of the free form in chloroform approached but did not equal that of the alcoholate in the same solvent. This may be due to a difference in the ethyl alcohol concentration present, although further work would be required to show this definitely. The properties of the three acetates are listed in Table III.

TABLE III

PROPERTIES OF THE FREE FORM, HYDRATE, AND ALCOHOLATE OF ALDEHYDO GALACTOSE PENTA-ACETATE

Form	M. p., °C.	$[\alpha]_D^{25}$, $CHCl_3$, U. S. P.
Aldehydo galactose penta-acetate	121	−25 (Initial)
Aldehydo galactose penta-acetate hydrate	125	+19.5 (Initial)
Aldehydo galactose penta-acetate ethyl alcoholate	133	− 0.5 (Initial)

Aldehydo galactose penta-acetate and its hydrate and alcoholate all readily reduce Fehling's solution on heating and their aqueous solutions give a strong Schiff test for the aldehydo group. Since the alcoholate reduces Fehling's solution, the ethyl alcohol cannot be present in any stable glycosidic linkage. The Schiff test given by the hydrate and alcoholate in aqueous solution denotes dissociation of the water and alcohol in combination. An aqueous solution of the alcoholate readily gave a crystalline semicarbazone, identical with that obtained in the same way from the free form. This semicarbazone showed a normal molecular weight by the Rast[9] method.

In the experimental work recorded in this paper, it was found convenient to prepare the aldehydo-galactose penta-acetate through the alcoholate, although it should also be possible to prepare the free form directly.

Further work on the synthesis and reactivity of the free aldehyde forms of sugar acetates is in progress in this Laboratory.

Experimental

Preparation of Galactose-ethylmercaptal.—The procedure of E. Fischer[10] always produced low yields when repeated in this Laboratory. The procedure to be described gave good results and is essentially that used by Levene and Meyer[8] in the preparation of mannose-ethylmercaptal except that more acid is required to dissolve the galactose. Fifty grams of galactose was placed in a 500-cc. glass-stoppered wide-mouthed bottle and dissolved at room temperature in 75 cc. of concentrated hydrochloric acid (sp. gr. 1.19). Fifty cc. of technical ethyl mercaptan was then added and the mixture vigorously shaken, releasing the pressure occasionally. After three to five minutes a definite temperature increase was noted. A little ice and ice water was then added. The con-

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[9] K. Rast, *Ber.*, 55, 1051 (1922).

[10] E. Fischer, *ibid.*, 27, **673** (1894).

tents of the bottle almost at once solidified to a mass of white crystals. More ice water was added and the mass filtered immediately, washing with a little ice water. The material was recrystallized from absolute alcohol and then from hot water; yield, 37 g.; m. p. 140–142°.

d-Galactose-ethylmercaptal Penta-acetate.—Fifty grams of galactose-ethylmercaptal was treated with 175 cc. of dry pyridine and cooled in ice. After nearly all of the mercaptal had dissolved, 250 cc. of acetic anhydride was gradually added. This addition caused the separation of a considerable quantity of solid. The mixture was allowed to stand in ice for about an hour and then kept at room temperature for eighteen hours. The undissolved material went into solution on occasional shaking. The solution was then poured into about 10 liters of ice water. The sirup thrown out readily crystallized; yield, 85 g., or 98%. Pure material was obtained by dissolving in methyl alcohol and adding water to opalescence, placing in the ice box, and from time to time adding more water until no further crystallization took place; yield, 81 g., m. p. 77–78°, $[\alpha]^{25}_{D}$ +9.8° in chloroform (U. S. P.) solution. After two further recrystallizations the melting point was 77 5–78.5° and the specific rotation in chloroform (U. S. P.) solution was +9.7° at a temperature of 25". The substance crystallizes in prismatic needles and is readily soluble in chloroform, ether, benzene, acetone and methyl alcohol; it is less soluble in ethyl alcohol and is practically insoluble in petroleum ether and water.

Anal. Subs., 0.2029: 20.4 cc. of 0.1 N KOH. Calcd. for $(C_2H_5S)_2C_6H_7O_5(CH_3CO)_5$: 20.4 cc. of 0.1 N KOH.

Aldehydo Galactose Penta-acetate Mono-ethyl Alcoholate.—The procedure followed in the preparation of aldehydo-glucose penta-acetate[1] was modified in order to obtain this compound. Twenty-five grams of galactose-ethylmercaptal penta-acetate (1 mol.) was dissolved in 90 cc. of acetone and 45 cc. of water added. The clear solution was held in a 3-necked round-bottomed flask provided with a good mechanical stirrer. An excess, 45–50 g., of washed and finely powdered cadmium carbonate was added and under rapid stirring a solution of 49 g (3.6 mols) of mercuric chloride dissolved in 72 cc. of acetone was gradually added. Stirring was maintained at room temperature for twenty-four hours, with occasional additions of small amounts of finely powdered cadmium carbonate. This was then filtered, an excess of fresh cadmium carbonate being placed in the suction flask, and the precipitate washed with acetone. The filtrate was then concentrated to dryness at 35° under reduced pressure and in the presence of excess cadmium carbonate. The residue was dried by adding absolute ethyl alcohol and distilling under reduced pressure, this being repeated. The residue was extracted with warm chloroform, filtered, 50 cc. of absolute alcohol added to the filtrate and the resulting solution evaporated at room temperature in a vacuum desiccator. The product crystallized completely during the course of this evaporation. An amount of 20.4 g. was obtained. This was dissolved in about four parts of hot absolute ethyl alcohol, norite added and the solution filtered from a small amount of insoluble material. On cooling slowly to room temperature crystallization began and was allowed to continue for eighteen hours at room temperature. The crystals were removed by filtration and washed with cold absolute ethyl alcohol; yield, 11 5 g; m. p 132–133". Further amounts of pure material were obtainable by repeated recrystallization from absolute ethyl alcohol of the material obtained by evaporating the mother liquor either to dryness or to low volume. From 72.9 g. of crude product, 56.2 g. of material melting at 132–133" was so obtained in six crops.

The substance crystallizes in diamond-shaped six-sided plates. It is soluble in warm water and in acetone, very soluble in chloroform, very slightly soluble in warm ether and practically insoluble in petroleum ether. The room temperature solubility in methyl alcohol is about 1.5 g. per 100 cc.; in ethyl alcohol, less than 1 g. per 100 cc.

It is soluble in about seven parts of boiling absolute ethyl alcohol. As the melting points of this substance and of the others here reported, were all very sensitive to slight impurities, this constant was used throughout this work as a criterion of purity. The melting point of the pure substance is **133–134°** when it is very rapidly heated to near the melting point. This melting point was unchanged by further recrystallization.

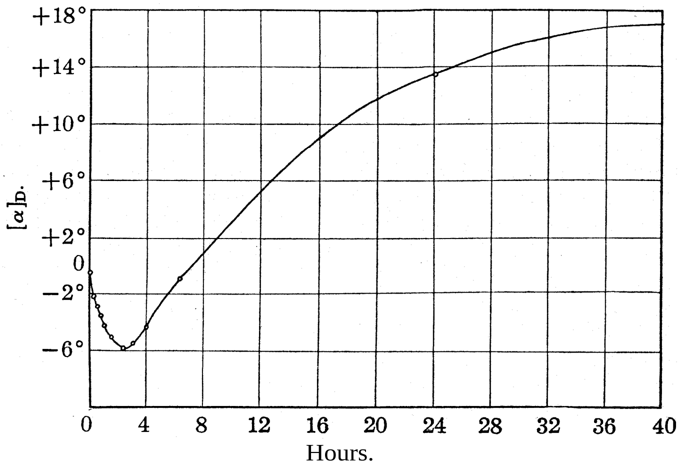

Fig. 1.—Rotation change of aldehydo galactose penta-acetate alcoholate in U. S. P. chloroform (Expt. 2).

TABLE IV

ROTATION CHANGES OF ALDEHYDO GALACTOSE PENTA-ACETATE ALCOHOLATE IN U. S. P. CHLOROFORM SOLUTION

1, 1.1 dm. λ, 5892 Å.

	Experiment 1 t, 25° c, 5.021			Experiment 2 t, 21° c, 5.013	
Time, min.	**a, degrees**	**[α]D, degree**	**Time, min.**	**a, degrees**	**[α]D, degrees**
0		−0.6[a]	0		− 0.5[a]
1.5	−0.05	−0.9	2	−0.05	− 0.9
5	− .10	−1.8	5	− .09	− 1.6
10	− .11	−2.0	10	− .11	− 2.0
15	− .14	−2.5	15	− .12	− 2.2
30	− .27	−4.9	30	− .16	− 2.9
45	− .36	−6.5	45	− .19	− 3.5
Hours			Hours		
1	− .37	−6.7	1	− .23	− 4.2
			1.5	− .28	− 5.1
			2.3	− .32	− 5.8
3	− .19	−3.4	3	− .30	− 5.5
			4	− .24	− 4.4
6	+ .28	+5.1	6.3	− .05	− 0.9
30	1.03	18.7	24	+ .74	+13.4
50	1.04	18.8	48	.92	16.7
			98	1.05	19.0
			124	0.92	16.7

[a] Interpolated.

The initial specific rotation of material of this purity in chloroform (U. S. P.) is −0.5". This rotation changes in the levo direction and then reverses sign and becomes dextro, reaching equilibrium at a specific rotation of +18°. This behavior is probably due to dissociation of the ethyl alcohol. The rotation change is plotted in Fig. 1 and the data are tabulated in Table IV. It was determined that this change was not mainly, at least, in the nature of a deep-seated isomerization involving an acetyl shift with the possible formation of a penta-acetate of lactal structure. The equilibrated chloroform solution was concentrated to dryness in a vacuum desiccator. The residue was but slightly changed in appearance from the original material, being slightly sticky, probably due to incomplete alcoholate formation. On one recrystallization from 95% ethyl alcohol, the original material was obtained in good yield. The melting point was 131–133" and was not depressed on admixture with known material of this same purity.

In methyl alcohol at room temperature the pure substance has no detectable initial rotation. The specific rotation gradually increases, reaching the equilibrium value of +14.5°. This rotation change is tabulated in Table V.

TABLE V

ROTATION CHANGES OF ALDEHYDO GALACTOSE PENTA-ACETATE ALCOHOLATE IN METHYL ALCOHOL

1, 2 dm. λ, 5892 Å.

Experiment 1	t, 25° c, 1.012		Experiment 2	t, 23° c, 1.015	
Time, min.	a, degrees	$[\alpha]_D$, degrees	Time, min.	a, degrees	$[\alpha]_D$, degrees
5	0	0	10	0	0
15	0	0	20	0	0
30	0	0	30	0	0
Hours			Hours		
5.5	+0.11	+5.5	3	+0.04	+2
9	.15	7.5	6	.08	4
24	.22	11.0	24	.23	11.5
49	.24	12.0	48	.29	14 5
76	.28	14.0	98	.31	15.5
147	.28	14.0	123	.28	14.0

The presence of ethoxyl in this compound was qualitatively determined by the procedure of Willstatter and Utzinger.[11] This consists in treating the substance with hydriodic acid and passing the alkyl iodide evolved into undiluted dimethylaniline. The resulting crystals were filtered, washed with cold acetone and recrystallized once from hot acetone. The crystals are very deliquescent and must be dried in a desiccator over sulfuric acid. The melting point was 136" and showed no depression on being mixed with an authentic specimen of dimethylethylphenylammonium iodide. The melting point of trimethylphenylammonium iodide is 232° (corr.)[12]

The alcohol in this compound dissociates very readily in solution, as the substance reduces hot Fehling's solution and gives a very strong Schiff aldehyde test. These tests were obtained by using dilute aqueous solutions of the substance formed by dissolving it in warm water and cooling to room temperature. The Schiff reagent used was that recommended by Alyea and Bäckström.[13] The substance also reacts instantaneously in aqueous solution with semicarbazide to form an insoluble semicarbazone.

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[11] R. Willstatter and M. Utzinger, *Ann.*, 382, 148 (1911).

[12] Max Phillips, THIS JOURNAL, 52, 793 (1930).

[13] H. N. Alyea and H. L. J. Backstrom, ibid., **51**, 97 (1929).

The substance is stable in the air and in a calcium chloride desiccator. It was not found possible to remove the alcohol by heating at various temperatures and under highly reduced pressure without decomposition of the acetate.

Anal. Subs., 0.2201: CO_2, 0.3970; H_2O, 0.1334. Subs., 0.3133: AgI, 0.1709. Subs., 0.1000: 11.41 cc. of 0.1 *N* KOH. Calcd. for $C_6H_7O_6(CH_3CO)_5C_2H_5OH$: C, 49.52; H, 6.47; OC_2H_5, 10.33; 11.46 cc. of 0.1 N KOH. Found: C, 49.19; H, 6.78; OC_2H_5, 10.46; 11.41 cc. of 0.1 N KOH; S, absent.

In the ethoxyl determination, a double Zeisel apparatus was used, the vapors from the first being passed through the second before being absorbed in the silver solution.

Aldehydo Galactose Semicarbazone Penta-acetate.—It was found possible to dissolve the alcoholate of aldehydo galactose penta-acetate in water and readily obtain the semicarbazone of this aldehyde from the solution. An amount of aldehydo galactose penta-acetate mono-ethyl alcoholate (m. p. 133–134") equal to 0.56 g. (1 mol) was dissolved in 5 cc. of hot water and the solution cooled to room temperature. A mixture of 0.12 g. (0.9 mol) of semicarbazide hydrochloride and 0.20 g. (1.6 mols) of potassium acetate was added to the solution and the whole shaken vigorously. After a few minutes a heavy crystallization took place. The mixture was allowed to stand overnight and then filtered and washed with cold water; yield, 0.43 g. (75%); m. p. 200–201" (corr.) with decomposition. On recrystallization from boiling water the substance crystallized in glittering, prismatic needles which in some cases were over one centimeter in length. The melting point was unchanged on one recrystallization and also on three recrystallizations. This melting point is identical with that of d-galactose semicarbazone,[14] but as both these values are more in the nature of decomposition points than true melting points, this fact need not be surprising. The substance is soluble in about 55 parts of boiling water, soluble in hot ethyl and methyl alcohol, and is very slightly soluble in chloroform, ether and acetone.

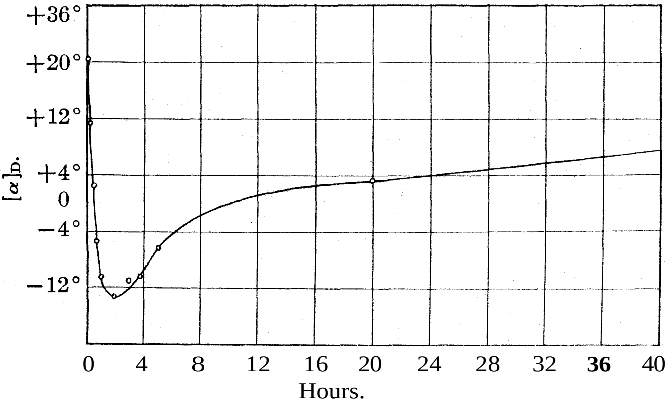

Fig. 2.—Rotation change of aldehydo galactose penta-acetate hydrate in U. S. P. chloroform (Expt. 2).

Anal. Subs., 0.2011: N_2, 16.97 cc. (752 mm., 25"). Subs., 0.1147: 13.0 cc. 0.1 *N* KOH. Calcd. for $C_7H_{10}O_6N_3(CH_3CO)_5$: N, 9.40; 12.8 cc. 0.1 N KOH. Pound: N, 9.23; 13.0 cc. 0.1 N KOH.

The acetyl determination was performed by dissolving the weighed sample (0.1 g.) in 20 cc. of boiling water, cooling rapidly to room temperature, and adding an equal

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[14] Maquenne and Goodwin, *Bull. soc. chim.*, [3] 31, 1075 (1904).

volume of 0.2 *N* potassium hydroxide before crystallization was initiated. The alkaline solution was then allowed to stand for one hour at room temperature and the excess alkali determined by titration with 0.1 N hydrochloric acid, using phenolphthalein indicator.

Molecular weight:[15] (Rast) 0.0102 g. of subs. in 0.1019 g. of camphor depressed the m. p. 9°. Mol. wt. calcd. for $C_{17}H_{25}O_{11}N_3$: 447. Found: 445.

Aldehydo Galactose Penta-acetate Monohydrate.—On several recrystallizations of the aldehydo galactose penta-acetate monoethyl alcoholate from boiling water the pure monohydrate was obtained. This substance crystallizes readily from water as prismatic

Table VI

Rotation Changes of Aldehydo Galactose Penta-acetate Hydrate in U. S. P Chloroform Solution

t, 27°. λ, 5892 Å.

Experiment 1 *l*, 2 dm. *c*, 2.011			Experiment 2 *l*, 1.1 dm. *c*, 4 003			Experiment 3 *l*, 1 dm. *c*, 2 011		
Time, min.	α, degrees	[α]D, degrees	Time, min.	α, degrees	[α]D, degrees	Time, min.	α, degrees	[α]D, degrees
0		+19.2[a]	0		+20.2[a]	5	+0.31	+15.4
2	+0.73	18 2	5	+0.76	17.3	10	.29	14.4
4	.71	17.7	7	.71	16.1	15	.22	10.9
6	.66	16.4	10	.63	14.3	20	.14	7.0
8	.62	15.4	13	.55	12.5	25	.11	5.5
10	.59	14.7	15	.52	11.8	30	.08	4.0
12	.55	13.7	17.5	.48	10.9	40	.02	1.0
14	.51	12.7	20	.44	10.0	55	− .08	− 4.0
						Hours		
16	.48	11.9	25	.32	7.3	1	− .14	− 7.0
20	.46	11.4	30	.10	2.3	1.2	− .16	− 8.0
25	.38	9.5	35	.01	0.2	3	− .21	−10.4
30	.30	7.5	41	− .16	− 3.6	5	− .28	−13.9
40	.17	4.2	45	− .25	− 5.7	18	0	0
			Hours					
50	.06	1.5	1	− .46	−10.5	23	+ .02	+ 1.0
Hours								
1	− .10	− 2.5	2	− .59	−13.4	30	.08	4.0
1.3	− .15	− 3.7	3	− .49	−11.1	45	.15	7.5
1.8	− .34	− 8.5	3.8	− .47	−10.7	54	.18	9.0
3	− .51	−12.7	5	− .28	− 6.4	71	.17	8.5
5	− .55	−13.7	20	+ .14	+ 3.2			
8	− .57	−14.2	46	.39	8.9			
12	− .29	− 7.2	56	.36	8.2			
27	+ .05	+ 1.2	73	.38	8.6			
47	.35	8.7						

[a] Interpolated.

Note.—The last values are somewhat uncertain due to evaporation of the chloroform on long standing and to an apparent decomposition that sometimes takes place after a period in this solvent.

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[15] We are indebted to Mr. Leonard Wise of this Laboratory for the determination of this molecular weight.

needles. The crystals are moderately soluble in chloroform, very slightly soluble in water at room temperature, but are soluble in hot water, very soluble in acetone and are practically insoluble in ether and petroleum ether. An aqueous solution of the substance readily reduced hot Fehling's solution and gave a strong Schiff test. The melting point was found to be 124–126°, on rapid heating to near the melting point, and this was unchanged by further recrystallization. Material of this purity showed an initial rotation in U. S. P. chloroform of +19.5°. This value changed to levo and then became dextro, becoming constant at +9°. These polarimetric data are plotted in Fig. 2 and are tabulated in Table VI.

Anal. Subs., 0.2110: CO_2, 0.3662; H_2O, 0.1174. Subs., 0.1000: 12.38 cc. of 0.1 *N* NaOH. Calcd. for $C_6H_7O_6(CH_3CO)_5\cdot H_2O$: C, 47.04; H, 5.93; 12.25 cc. of 0.1 N NaOH. Found: C, 47.32; H, 6.23.

Aldehydo Galactose Penta-acetate.—On several recrystallizations of the aldehydo galactose penta-acetate mono-ethyl alcoholate from hot toluene, the pure free aldehyde form of the penta-acetate was obtained. This substance readily crystallizes from toluene

TABLE VII

ROTATION OF ALDEHYDO GALACTOSE PENTA-ACETATE

t, 27°. λ, 5892 Å.

Expt. 1, U. S. P. $CHCl_3$ *l*, 1.1 dm. *c*, 4.001			Expt. 2, U. S. P. $CHCl_3$ *l*, 1.1 dm. *c*, 4.005			Expt. 3, $CHCl_2$—$CHCl_2$ *l*, 1 dm. *c*, 3.990		
Time, min.	α, degrees	$[\alpha]_D$, degrees	Time, min.	α, degrees	$[\alpha]_D$, degrees	Time, min.	α, degrees	$[\alpha]_D$, degrees
0		−25[a]	0		−25.5[a]	3	−0.65	−16.3
3	−0.97	−22.0	2	−1.08	−24.5	5	− .65	−16.3
4	− .93	−21.1	3	−1.00	−22.7	10	− .63	−15.8
6	− .92	−20.9	4	−1.01	−23.0	15	− .64	−16.0
10	− .77	−17.5	6	−0.93	−21.1	30	− .62	−15.5
16	− .68	−15.5	8	− .87	−19.8	Hours		
20	− .66	−15.0	10	− .87	−19.8	1	− .64	−16.0
27	− .57	−13.0	15	− .81	−18.4	2	− .65	−16.3
35	− .43	− 9.8	20	− .72	−16.4	6.5	− .65	−16.3
45	− .35	− 8.0	30	− .61	−13.9	21.5	− .66	−16.5
Hours			45	− .35	− 8.0	65.5	− .65	−16.3
1	− .28	− 6.4	Hours				Av.	−16.1
1.25	− .18	− 4.1	1	− .19	− 4.3			
1.5	− .08	− 1.8	1.5	− .10	− 3.3			
1.75	− .04	− 0.9	2	− .01	− 0.2			
2	+ .04	+ 0.9	2.5	+ .10	+ 2.3			
2.5	.08	1.8	3	+ .23	+ 5.2			
3	.15	3.4	8	+ .35	+ 8.0			
4.3	.29	6.6						
6	.36	8.2						
7	.38	8.6						
22	.46	10.5						
41	.43	9.8						

[a] Interpolated.

NOTE.—(a) The last values in Expts. 1 and 2 are somewhat uncertain due to evaporation of the chloroform on long standing and to an apparent decomposition that sometimes takes place after a period in this solvent. (b) A second set of readings in acetylene tetrachloride solutions gave the average value of −16.3° for the specific rotation in this solvent.

as very characteristic clusters of elongated prisms. The crystals are very soluble in chloroform, soluble in acetone and hot water, slightly soluble in alcohol and benzene at room temperature, but more soluble in the warm, very slightly soluble in ether and practically insoluble in petroleum ether. An aqueous solution of the substance readily reduced Fehling's solution when heated and gave a strong Schiff test. The melting point was found to be 120–121°, unchanged by further recrystallization. Material of this purity showed an initial rotation in U. S. P. chloroform of −25°, changing to +10°. That this change was very probably due to combination with the ethyl alcohol in the U. S. P. chloroform was shown by the fact that the rotation was constant in pure acetylene tetrachloride solution, $[\alpha]_D^{27}$, −16° (Table VII). Before use the acetylene tetrachloride was washed with sodium bicarbonate solution to remove the acidity present in this solvent on standing, then with water, and the liquid then dried and distilled. The polarimetric data obtained with this compound are tabulated in Table VII.

A mixed melting point of the compound, m. p. 120–121°, with the first form of galactose penta-acetate, m. p. 142°, gave the value 107–111°. The other three forms of galactose pentaacetate melt below 100°.[16] The semicarbazone was prepared from this substance in accordance with the previously recorded procedure, and was found to have the same melting point as the semicarbazone prepared from the alcoholate and showed no melting-point depression on being mixed with material from this source.

That the penta-acetate was a derivative of galactose was determined by identification of the mucic acid formed from it by oxidation. An amount of 0.5 g. of the penta-acetate, m. p. 120–121°, was oxidized with nitric acid according to the Kent–Tollens[17] procedure. After two recrystallizations performed by dissolving the substance in 10% sodium hydroxide and adding 50% hydrochloric acid in slight excess, the crystals of mucic acid melted at 213–214° (corr.) with decomposition and slight preliminary darkening.

Anal. Subs., 0.2429: CO_2, 0.4374; H_2O, 0.1291. Subs., 0.1000: 12.80 cc. of 0.1 *N* NaOH. Calcd. for $C_6H_7O_6(CH_3CO)_5$: C, 49.21; H, 5.68; 12.81 cc. of 0.1 *N* NaOH. Found: C, 49.11; H, 5.95.

The writer wishes to acknowledge his indebtedness to Miss Winifred Robinson for assistance in the preliminary isolation of aldehydo galactose alcoholate.

Summary

1. A fifth form of d-galactose penta-acetate has been prepared in pure condition.

2. Evidence is given that this compound possesses the open-chain, free aldehyde structure and the name aldehydo galactose penta-acetate is suggested for this substance.

3. The hydrate and ethyl alcoholate of this compound have been prepared in pure form and evidence is given that they represent the aldehydrol and ethyl-hemi-acetal structures, respectively.

4. The crystalline semicarbazone of aldehydo galactose penta-acetate has been prepared in pure form.

COLUMBUS, OHIO

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[16] Cf. Table I.

[17] A. W. van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren," 1920, p. 103,

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF WISCONSIN, AND THE OFFICE OF CEREAL CROPS AND DISEASES, BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE ACTION OF WEAK MINERAL ACIDS ON URONIC ACIDS[1,2]

BY KARL PAUL LINK AND CARL NIEMANN

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Introduction

When either d-glucuronic or d-galacturonic acid is heated with 12.0% hydrochloric acid, decomposition follows with the liberation of carbon dioxide, furfuraldehyde and water, according to the equation

$$C_6H_{10}O_7 = C_5H_4O_2 + 3H_2O + CO_2$$

Conjugated uronic acids, the so-called polyuronides found in pectins, gums, alginic acids, the specific polysaccharide substances of certain micro-organisms, and other plant materials also yield carbon dioxide when heated with 12.0% hydrochloric acid. The carbon dioxide liberated according to the above reaction serves as a basis for the accurate determination of these substances by any one of several methods.[3] Before it had been established with certainty that the plant gums contain uronic acids, Zeisel and Konschegg reported that gum acids not only yield large quantities of carbon dioxide when heated with 12.0% hydrochloric acid, but that they also produce considerable amounts of carbon dioxide when the acid is more dilute. This observation of Zeisel and Konschegg was originally published in the first edition of Wiesner, "Die Rohstoffe des Pflanzenreichs," Vol. III, p. 87. Reference is again made to this obscure observation in the latest edition of Wiesner.[4] Apparently they did not publish this observation in a chemical journal; as a result this important fact has been overlooked by many workers even after it had been demonstrated with certainty that plant gums contain uronic acids.[5] Con-

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[1] Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

[2] Part of this research was done by one of us (K. P. L.) during 1925–1927 while a Fellow of the International Education Board, posted at the time at the University of Zürich, Switzerland. The author wishes to acknowledge his indebtedness to Professor Paul Karrer, Director of the Institute of Chemistry, University of Zürich, for the privilege of extending the research while a student in his laboratory, and for the kindly advice and help received. To the Board of Directors of the International Education Board, New York City, the author wishes to extend his thanks for the Fellowship grant which enabled him to work in the laboratory mentioned.

[3] (a) Tollens and Lefèvre, *Ber.*, 40, 4513 (1907); also (b) Dickson, Otterson and Link, THIS JOURNAL, 52, 775 (1930), where reference is made to the various methods in, use for the determination of uronic acids.

[4] Wiesner, "Die Rohstoffe des Pflanzenreichs," Engelmann, Leipzig, 1927, Vol. I, 4th ed., p. 974.

[5] For early literature on this subject see Wiesner "Die Rohstoffe des Pflanzenreichs," and Czapek, "Biochemie der Pflanzen," 3d ed. Vol. I, p. 673, Gustav Fischer, Jena, 1922.

sequently the many articles which have appeared on uronic acids and polyuronides up to within very recent times reveal the very significant fact that whenever the experimental procedure involves a prolonged weak mineral acid hydrolysis, the subsequent yields of the free acids obtained are invariably either very small or nil.

In general polyuronide substances are hydrolyzed only very slowly by weak mineral acids, consequently there is ample opportunity for the destruction of the free acids liberated during the hydrolysis. Some of the many papers wherein the destructive action of weak mineral acids has caused experimental difficulties, whose actual sources were not recognized, have been cited in an article by one of us in THIS JOURNAL.[3b]

Although most investigators have not been cognizant of the fact that uronic acids are destroyed by weak mineral acids, recently some investigators have reported their observations on this subject. Thus Heidelberger and Goebel in a study of the aldobionic acid obtained from the specific polysaccharide of Type III Pneumococcus stated that when the aldobionic acid was hydrolyzed in 1 N sulfuric acid for twenty hours, half of the molecule (the sugar acid) was largely destroyed.[6] Butler and Cretcher in a study of the composition of gum arabic obtained an aldobionic acid which on hydrolysis with 5% sulfuric acid yielded d-galactose. However, the acidic fraction was present in too small amounts to be identified. This was due to the fact that under the conditions of the hydrolysis the uronic acid was largely destroyed. Control experiments indicated that the aldobionic acid was decomposed to the extent of about 44%.[7] Heidelberger and Kendall[8] obtained an aldobionic acid from gum arabic which they oxidized to the dicarboxylic acid. When this acid was hydrolyzed in 1 N sulfuric acid for eighteen hours, 28.0% of the glucuronic acid formed was decarboxylated. In their study on the alginic acid from *Macrocystis Pyrifera,* Nelson and Cretcher[9] state, "the hydrolysis of alginic acid with dilute sulfuric acid of various concentrations was attempted but soon abandoned because of the simultaneous loss of carbon dioxide." Several years ago, one of us (K. P. L.) devised a method for the preparation of galacturonic acid from lemon pectic acid, and glucuronic acid from cherry gum. While engaged on this study it was necessary to determine what strength of mineral acid would effect a maximum hydrolysis of the source material and at the same time produce a minimum destruction of the liberated uronic acid. At first many experiments were conducted with various concentrations of mineral acids below 1.0%. It was found that the source material hydrolyzed so slowly that most of the liberated uronic

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[6] Heidelberger and Goebel, *J. Biol. Chem.*, *70*, 613 (1926); *ibid.*, 74, 613 (1927).

[7] Butler and Cretcher, THIS JOURNAL, 51, 1519 (1929).

[8] Heidelberger and Kendall, *J. Biol. Chem.*, *84*, 641 (1929).

[9] Nelson and Cretcher, THIS JOURNAL, 51, 1914 (1929).

acid was destroyed as rapidly as it was formed, It was found necessary to use higher concentrations of the mineral acids to hydrolyze the material effectively, thereby causing the ratio of uronic acid liberated to the uronic acid destroyed to approach an optimum value.

In this paper we present the results obtained by the action of mineral acids of concentrations in common use in the hydrolysis of pectins, hemicellulose, gums, gum acids and other plant substances. The effect of various dilute concentrations of hydrochloric acid and sulfuric acid were ascertained on the following substances; (a) crystalline d-glucuronic and d-galacturonic acid, (b) gum arabic and a gum arabic acid both of which contain a polyglucuronide complex, (c) lemon pectin acid which contains a polygalacturonide, (d) an aldobionic acid from cherry gum wherein one half of the molecule is a uronic acid

Experimentation

The experiments were conducted on the various substances following the procedure recently described.[3b] The heating was conducted for the prescribed periods at a bath temperature of 135–140°, which was found to keep the solution in the reaction flask at constant ebullition, provided boiling chips were used. The hydrolysis was terminated by removing the electric heater and oil-bath. The aspiration of carbon dioxide-free air through the apparatus was continued for an additional thirty minutes so as to remove the carbon dioxide remaining in the reaction flask. After this had been accomplished, the amount of barium hydroxide utilized during the run was determined in the usual manner. All of the experiments reported below represent the average of duplicate analyses that agreed to within 0.50%.

The Decarboxylation of d-Galacturonic Acid under Various Conditions.—Pure d-galacturonic acid, m. p. **159°**, $[\alpha]^{20}_{D}$ +53.40 in water, prepared from lemon pectic acid by a method soon to be published was used in these experiments.

Action of 2.5% Sulfuric **Acid.**[10]—**Three-tenths** g. heated for two hours liberated **0.0088 g.** of carbon dioxide which is equivalent to a destruction of 12.9%; **0.30** g. heated for four hours liberated **0.0169** g. of carbon dioxide, which represents a destruction of 24.75%.

Action of 1 *N* Sulfuric **Acid.**[11]—**Three-tenths** g. heated for fifteen hours liberated **0.0396 g.** of carbon dioxide, equivalent to a destruction of **58.10%**.

Action of 2.0% Hydrochloric **Acid.**[12]—**Three-tenths** g. heated for one and one-half

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[10] Two and one-half per cent. sulfuric acid is frequently used in the hydrolysis of hemicelluloses, the time interval varying from two to four hours.

[11] **1** *N* sulfuric acid is used most extensively in the hydrolysis of gum acids, the time interval being about fifteen hours.

[12] Whenever hydrochloric acid is used in the hydrolysis of hemicellulose the time of the hydrolysis and the concentration of the acid are usually less than when sulfuric acid is employed. The hydrolytic action of dilute hydrochloric acid is more drastic than that of weak sulfuric acid. Consequently in the hydrolysis of hemicellulose both the concentration and the length of the hydrolysis are decreased.

hours liberated 0.0094 g. of carbon dioxide, equivalent to a destruction of 13.65%; 0.30 g. heated for three hours liberated 0.0197 g. of carbon dioxide, equivalent to a destruction of 29.30%.

The Decarboxylation of d-Glucuronic Acid under Various Conditions.—Pure *d*-glucuronic acid, m. p. 156°, $[\alpha]_D^{20}$ +34.0 in water, prepared from gum arabic was used in these experiments.

Action of 2.5% Sulfuric Acid.—One-quarter g. heated for two hours liberated 0.0056 g. of carbon dioxide, equivalent to a destruction of 9.66%; 0.25 g. heated for four hours liberated 0.0096 g. of carbon dioxide, equivalent to a destruction of 18.20%.

Action of 1 N Sulfuric Acid.—One-quarter g. heated for two hours liberated 0.0078 g. of carbon dioxide, equivalent to a destruction of 13.72%; 0.25 g. heated for three hours liberated 0.0110 g. of carbon dioxide, equivalent to a destruction of 19.40%; 0.25 g. heated for four hours liberated 0.0146 g. of carbon dioxide, equivalent to a destruction of 24.60%; 0.25 g. heated for fifteen hours liberated 0.0326 g. of carbon dioxide, equivalent to a destruction of 57.20%.

Action of 2.0% Hydrochloric Acid.—Three-tenths g. heated for one and one-half hours liberated 0.0091 g. of carbon dioxide, equivalent to a destruction of 13.35%; 0.30 g. heated for three hours liberated 0.0197 g. of carbon dioxide, equivalent to a destruction of 28.80%.

The Destruction of d-Glucuronic Acid in the Course of Its Preparation from Gum Arabic.—Weinmann[13] has recently published the most successful method for the preparation of d-glucuronic acid from a naturally occurring plant substance. One gram of gum arabic with a uronic acid content of 17.60% was hydrolyzed in 2.0% hydrochloric acid for one and one-half hours. During this time 0.0048 g. of carbon dioxide was liberated, equivalent to a destruction of 2.11% of the total gum or 12.0% of the total quantity of glucuronic acid present in the original gum.

One gram of gum acid, prepared from the gum arabic employed above according to Weinmann's method (uronic acid content of the gum acid 27.70%) was hydrolyzed in 1 *N* sulfuric acid for fifteen hours, whereupon 0.0349 g. of carbon dioxide was liberated, equivalent to a destruction of 15.28% of the gum acid or 55.05% of the total quantity of glucuronic acid present in the gum acid.[14]

The Destruction of d-Galacturonic Acid in the Course of Its Preparation from Lemon Pectic Acid.—One g. of lemon pectic acid (galacturonic acid content 88.0%) was hydrolyzed for fifteen hours with 2.0% sulfuric acid; in the course of the above reaction 0.0677 g. of carbon dioxide was liberated, equivalent to a destruction of 27.80% of the pectic acid molecule or 33.85% of the total amount of the galacturonic acid present.

The Destruction of the Uronic Acid Residue of an Aldobionic Acid in I N Sulfuric Acid.—The barium salt of an aldobionic acid isolated from cherry gum was used in this experiment. The free acid has not been obtained in a crystalline condition, although the barium salt is apparently pure, since it liberates one molecular equivalent of carbon dioxide when heated with 12.0% hydrochloric acid and has the correct barium content; 0.5958 g. of the barium salt equivalent to 0.50 g. of the free acid was hydrolyzed for fifteen hours, whereupon 0.0330 g. of carbon dioxide was liberated, equivalent to a destruction of 53.00%, since complete decarboxylation gave 0.0627 g. of carbon dioxide.

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[13] Weinmann, *Ber.*, 62, 1637 (1929).

[14] The yield of d-glucuronic acid from gum arabic by Weinmann's method is approximately 50 g. of the acid from 1 kilo of the gum. Calculated on the basis of the uronic acid content of the gum this is equivalent to 28.50% of the total amount of glucuronic acid theoretically available. Accounting for the inevitable hydrolytic destruction, the maximum yield obtainable is 40% of the uronic acid present in the gum,

Discussion

In view of the fact that free uronic acids are destroyed by weak mineral acids, an inevitable destruction takes place when they are prepared from their parent sources, *i. e.*, gum arabic, gum acids, pectic acids, aldobionic acids (of the type recently obtained from gums) and various microorganisms. Polyuronide substances are in general quite resistant to the action of weak mineral acids. Consequently, when the free uronic acids are sought, the hydrolytic procedure should be directed toward the attainment of a rapid hydrolysis of the parent substance in order to minimize the destruction of the free acid. The general practice of using 1 N sulfuric acid in preference to 1 N hydrochloric acid when a prolonged hydrolytic procedure is involved is to be recommended.

The following factors enter into a consideration of the destruction of uronic acids by weak mineral acids; the strength of the acid, the temperature, the. concentration of the uronic acid in the hydrolytic medium and the length of exposure of the free acids to the hydrolytic agent. Concentrations of hydrochloric or sulfuric acid above 5.0% are so effective in their decarboxylating action that the employment of these acids in the hydrolysis of polyuronides is not to be recommended. The concentration of the mineral acid employed should be less than 5%, but more than 2%, since the hydrolysis of most polyuronides proceeds too slowly in concentrations of 2.0% or less with the result that the free uronic acid is destroyed almost as rapidly as it is liberated. At temperatures below 100° the destructive action of weak mineral acids upon uronic acids decreases rapidly (unpublished data). However, it is difficult to effect the hydrolysis of the polyuronide substances at these temperatures. Many experiments were conducted in an attempt to hydrolyze polyuronides below 100°. However, the yields of the free acid were so small that temperatures below 100° proved to be impracticable. For this reason we have not presented the experimental results attained with various concentrations of weak mineral acids at temperatures ranging from 65–100°.

The rate of decarboxylation of a uronic acid by the action of weak mineral acids also varies with the concentration of the uronic acid present. Thus in the case of the decarboxylation of d-glucuronic acid in 1 N sulfuric acid, 13.72% of an original sample of 0.25 g. in 100 cc. was destroyed in two hours and 24.60% destroyed at the end of four hours. From the rate of decarboxylation during the first four hours, complete decarboxylation of the sample should have been effected in the course of approximately sixteen hours. However, at the end of fifteen hours only 57.20% had been destroyed, based upon the amount of carbon dioxide liberated.

We have observed that reversion products of the uronic acids are readily formed in weak mineral acid solutions. The higher the initial concentration of the uronic acids, the greater and the more rapid is the formation of the reversion products. These reversion products are quite stable toward weak acids, for in an hydrolysis conducted with 1 *N* sulfuric acid for over one hundred hours, all of the carbon dioxide theoretically obtainable from a sample of d-galacturonic acid had not been liberated, although free d-galacturonic acid was no longer present. The formation of these reversion products helps to explain the fact that the decarboxylation of a given amount of uronic acid in any weak mineral acid is not a linear function referred to time. In addition, the action of weak mineral acids does not appear to proceed quantitatively according to the equation

$$C_6H_{10}O_7 = C_5H_0O_2 + 3H_2O + CO_2$$

as is the case when the concentration of the acid is 12.0%. Apparently some side reactions occur, as the quantity of furfural produced is less than the amount expected on the basis of the carbon dioxide produced. A substance is produced in the course of the reaction which is not furfuraldehyde, but it reduces Fehling's solution readily at room temperature, and gives the various tests for pentose sugars. The nature of this substance is being studied for it appears to be not without significance since it seems to be a furan derivative.

It has been postulated repeatedly by DeChalmont,[15] Spoehr,[16] Haworth,[17] Ehrlich[18] and others that the pentose sugars arise from uronic acids by direct decarboxylation. Thus xylose would be formed from glucose, and arabinose from galactose. The formation of the aforementioned furan product by the action of dilute mineral acids is indicative of the fact that uronic acids can apparently be decarboxylated *in vitro* without the reaction proceeding to the furfuraldehyde stage. When furfuraldehyde is formed from a uronic acid by the action of 12% hydrochloric acid, it is assumed that a pentose sugar is intermediate in this reaction. According to Nelson and Cretcher[8] the pentoses reported by Kylin, Hoagland and Lieb (*loc. cit.*) to be present in the alginic acid from *Macrocystis pyrifera* might be regarded as having been formed by decarboxylation of the uronic acid that comprises this alginic acid.

In concluding, it should be stated that the methods now in use in plant physiological and plant biochemical studies for the determination of pectin substances and hemicelluloses are inaccurate due to the error introduced through the destruction of the uronic acids that comprise part of the molecule of these substances. This is particularly the case in the estimation of the hemicelluloses, which is accomplished by determining the total reducing power after an acid hydrolysis, which is usually done

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[15] DeChalmont, *Am. Chem.* **J., 16,** *610* **(1893);** *Ber.,* **27,2722 (1894).**

[16] **Spoehr,** *Carnegie Inst.* **Pub., No. 387, 42, 75 (1917).**

[17] Haworth, **J.** *Soc. Chem. Ind.,* **28, 295T (1927);** *Helv. Chim. Acta,* 11, **534 (1928).**

[18] Ehrlich **and Schubert,** *Biochem. Z.,* **203,343 (1929).**

with 2.5–5% hydrochloric or sulfuric acid.[19] It has been shown by O'Dwyer,[20] Schmidt[21] and co-workers, Schwalbe and Feldtmann[22] and others, that hemicelluloses contain uronic acids. A hemicellulose preparation from the maize plant has been obtained that contains d-glucuronic acid.[23]

The authors wish to acknowledge their indebtedness to Dr. Allan Dickson for assistance rendered during the course of this work.

Summary

d-Glucuronic and *d*-galacturonic acids are decarboxylated when heated with either hydrochloric or sulfuric acid of concentrations below 5.0%. In the course of the preparation of these acids from their parent polyuronide substances by hydrolytic procedures, an inevitable destruction occurs. This destruction accounts for the low yields that are usually obtained in the course of the preparation of the uronic acids from their natural source materials, and also contributes to an error in the course of the determination of hemicellulose and pectin in plant physiological studies. Besides carbon dioxide, furfuraldehyde and some reversion products, the action of dilute mineral acids produces a furan derivative whose nature has not been determined.

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. V. THE IDENTITY OF ISOTUBAIC AND ROTENIC ACIDS

BY H. L. HALLER AND F. B. LAFORGE

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When an alcoholic potassium hydroxide solution of rotenone is refluxed for several hours, an acid is obtained in a yield of about 5% which represents approximately half of the rotenone molecule and which is known as tubaic acid. Kariyone, Kimura and Kondo[1] have established the empirical formula $C_{12}H_{12}O_4$ for tubaic acid and this formula has been confirmed by Takei.[2]

Tubaic acid possesses the properties of a phenolcarboxylic acid. It shows an acid reaction to litmus and requires 1 mole of alkali for its neu-

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[19] Report of Committee on Methods, *Plant Physiology,* 2, 93–95 (1927).

[20] O'Dwyer, *Biochem.* J., 17, 501 (1923); 19, 694 (1925); 20, 656 (1926).

[21] Schmidt, Meinel and Zintl, Ber., 60, 503 (1927).

[22] Schwalbe and Feldtmann, *ibid.,* 58, 1534 (1925).

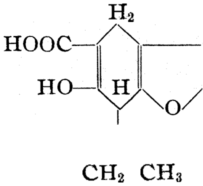
[23] Unpublished data of the senior author to which reference has been made in THIS JOURNAL, 51, 2506 (1929).

[1] Kariyone, Kimura and Kondo, *J. Pharm. Soc.* (Japan), No. 514, 1094 (1924); *ibid.,* No. 518, 377 (1926).

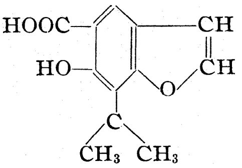
[2] Takei, *Ber.,* 61, 1003 (1928).

tralization. In alcohol solution it gives a violet color with ferric chloride, and it forms an acetyl derivative. It yields a dimethyl derivative, in which one methyl group is readily saponifiable, and the other is in the form of a methoxyl, replacing the original phenol group. Tubaic acid contains a double bond which is readily reduced with colloidal palladium and hydrogen. It contains no methoxyl group. All attempts to bring the fourth oxygen atom into reaction so far have failed. Tubaic acid yields acetic acid on oxidation in aqueous solution with permanganate, whereas dihydrotubaic acid and rotenic acid, which will be discussed below, yield isobutyric acid.[3]

A tentative structural formula for tubaic acid (I) has been proposed recently by Takei, Koide and Miyajima.[3]



I



II

Tubaic acid is converted by fusion with potassium hydroxide into an isomeric compound known as rotenic acid, for which Takei, Koide and Miyajima have advanced the structural formula II. Rotenic acid can also be prepared by fusing rotenone with solid potassium hydroxide.

According to the Japanese investigators the conversion of tubaic acid into rotenic acid is brought about by a migration of two hydrogen atoms, as a result of which the iso-allyl group is converted into an isopropyl group and a more stable conjugated system is formed.

When rotenone is dissolved in concentrated sulfuric acid and the resulting solution is diluted with water, or when rotenone is boiled with 50% sulfuric acid, an isomer of rotenone is obtained which is known as isorotenone.[2] So far as we know neither Takei nor Butenandt has proposed an explanation of the difference in structure between rotenone and isorotenone. It has been suggested by one of the writers[4] that the iso-allyl group in rotenone has been converted into a trimethylene ring in the formation of isorotenone.

In the course of our investigations on the structure of rotenone we have prepared isotubaic acid by refluxing an alcoholic potassium hydroxide solution of isorotenone and isolating the resulting acid in the same manner that was described for the preparation of tubaic acid.[5] A product melting

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[3] Takei and Koide, *Bull. Inst. Phys. Chem. Res.*, *8*, *No.* 6, 64 (1929); also in *Ber.*, 62, *3030* (1929); Takei and Miyajima, *Bull. Inst. Phys. Chem. Res.*, *8*, *No.* **6,** 61 (1929).

[4] LaForge and Smith, THIS JOURNAL, 51, 2574 (1929).

[5] Takei, *Biochem. Z.*, 157, 1 (1925).

at 186° was obtained which in alcoholic solution gave a blue color with ferric chloride. Rotenic acid[5] according to Takei melts at 182° and gives a blue color in alcoholic solution with ferric chloride. We have prepared rotenic acid by the procedure described by Takei and found its melting point to be 182°. The mixed melting point of a mixture of isotubaic acid and rotenic acid was 185°. G. L. Keenan of the Food, Drug and Insecticide Administration, U. S. Department of Agriculture, has determined the optical properties of isotubaic acid and rotenic acid and was unable to find any difference between them. The acetyl derivative of isotubaic acid was prepared and found to melt at 156°. According to Takei,[2] the acetyl derivative of rotenic acid melts at 155°.

Isotubaic acid is also obtained when tubaic acid is refluxed with 50% sulfuric acid.

It is a surprising fact that rotenic acid (isotubaic acid) is obtained from derritol by the alkali fusion process, details of which will be presented in another communication to follow shortly.

Since isotubaic acid and rotenic acid are identical,[6] the change which takes place when rotenone is converted into isorotenone is the same as when rotenic acid is produced from tubaic acid. Accordingly the theory of the mechanism for the transformation of rotenone into isorotenone advanced by one of the writers or the explanation suggested by Takei and Koide for the change taking place in the conversion of tubaic acid into rotenic acid must be altered. The investigation is being continued.

Experimental

Isorotenone.[2]—Ten grams of rotenone was added to a solution of 330 cc. of concentrated sulfuric acid in 600 cc. of water and the mixture was refluxed for eight hours. After standing at room temperature overnight, the solution was filtered, the isorotenone was washed free of sulfuric acid and then recrystallized from alcohol; it melted at 183°. An equal volume of water was added to the alcoholic filtrate and the precipitate was filtered off and dried. It melted at about 100°. It has not yet been identified.

Isotubaic Acid.—Ten grams of isorotenone was added to a solution of 6 g. of potassium hydroxide in 200 cc. of alcohol. The solution was refluxed for three hours, diluted with water and acidified with dilute sulfuric acid. The precipitate was filtered off and extracted with a 5% aqueous solution of sodium carbonate. This solution was acidified with dilute sulfuric acid and the isotubaic acid was filtered off. It may be recrystallized from dilute alcohol solution, dilute acetic acid or from ether–petroleum ether. It melted at 186°. Mixed with rotenic acid it melted at 185°. For analysis it was dried to constant weight at 110°.

Anal. Subs., 0.0632: CO_2, 0.1518; H_2O, 0.0321. Calcd. for $C_{12}H_{12}O_4$: C, 65.42; H, 5.50. Found: C, 65.53; H, 5.68.

Mr. Keenan states, "Isotubaic and rotenic acids were found to be identical in so far as partial optical data (immersion method) could determine. Both substances

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[6] The identity of isotubaic and rotenic acids is reported by Butenandt [*Ann.*, 477, 245 (1930)] and by Takei, Koide and Miyajima [Ber., **63**, 508 (1930)] in recent articles which came to our attention after this paper had been prepared for publication.

were rod-like in habit with a minimum index of refraction of **1.445,** which may be considered as α for the acids. The other indices of refraction were found to be very high and not measurable by the liquids available."

Rotenic Acid.—Ten grams of rotenone was intimately mixed with 40 g. of powdered potassium hydroxide and heated in an oil-bath to 180–200°. When fusion was completed, the cooled mass was dissolved in water and the solution was acidified with dilute sulfuric acid. The precipitate was filtered off and dissolved in ether; the ether solution was dried over anhydrous sodium sulfate. The ether was removed and the residue was extracted with petroleum ether, from which the rotenic acid separated on cooling. It melted at 182°. A mixture of rotenic acid and isotubaic acid had a melting point of 185°. The optical data as determined by Mr. Keenan of the Food, Drug and Insecticide Administration were the same as for isotubaic acid.

Isotubaic Acid from Tubaic Acid.—One-tenth gram of tubaic acid was added to 5 cc. of 50% sulfuric acid, and the mixture was refluxed for one hour. After cooling, the solution was exactly neutralized with dilute sodium hydroxide and then extracted with ether. After removal of the ether, the acid was recrystallized from ether–petroleum ether. It gave the characteristic blue color of isotubaic acid in alcohol solution with ferric chloride.

Summary

Isotubaic acid was prepared from isorotenone and was found to be identical with rotenic acid.

The change which occurs when rotenone is converted into isorotenone involves the same groupings as when rotenic acid is formed from tubaic acid.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

THE OXIDATION OF INOSITE WITH NITRIC ACID

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The object of this investigation was an attempt to clear up the apparently contradictory results obtained by different investigators in the oxidation of inosite with nitric acid. Maquenne[1] oxidized inosite with three to five times its weight of fuming or concentrated nitric acid in an open dish, on a water-bath. He obtained upon evaporating to dryness, a white residue which was washed with absolute alcohol to remove the trace of oxalic acid formed, and then taken up in water and evaporated on the water-bath. The solution immediately began to turn brown, and soon a brown precipitate which he believed to be tetrahydroxyquinone separated. A solution of the oxidized material when treated with barium chloride, gave barium rhodizonate, which he identified by its red color. When the oxidized material, in water solution, was treated with sodium carbonate, a greenish-black powder separated, which he reported as a mixture of the di-sodium salts of tetrahydroxyquinone and rhodizonic acid. By acidifying he again

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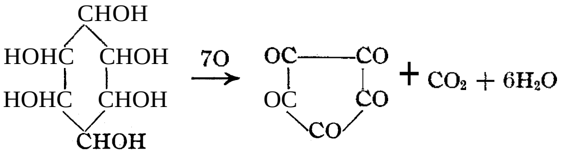
[1] Maquenne, *Compt. rend.*, 104, 298 (1886).

obtained tetrahydroxyquinone, and on treatment with concentrated nitric acid, triquinoyl was formed. This last compound was isolated and analyzed. By warming a solution of triquinoyl in the presence of potassium hydroxide, crystals of the di-potassium salt of croconic acid were obtained.

Contardi[2] carried out the oxidation of inosite in essentially the same manner, using fuming nitric acid. However, he reported no oxalic acid, but obtained a white residue which remained white even after taking up in water and evaporating the solution to dryness. This material he claimed was pure leuconic acid. He crystallized the material from nitric acid and thereby obtained a white crystalline substance which analyzed to give the correct percentage composition for leuconic acid with five molecules of water of crystallization. The oxidized material was also treated with hydroxylamine, and a substance was obtained which was not crystalline, and which he was unable to purify because of its insolubility in all solvents except bases. This compound, when analyzed, gave the correct percentage of nitrogen to correspond with the penta-oxime of leuconic acid. On the basis of these results Contardi concluded that the oxidation of inosite with nitric acid produced only leuconic acid, and proceeded as follows



Inosite Leuconic acid

Since the percentage composition of rhodizonic acid, tetrahydroxyquinone, triquinoyl, croconic acid and leuconic acid may be almost equal, depending upon the amount of water of crystallization which each compound may contain, the results of Contardi's analysis of his crystalline compound seemed hardly sufficient ground for the conclusion that the material was only leuconic acid. The objection is increased when we consider that he had no method for establishing the purity of his product. Neither did it seem logical to place very much weight upon the fact that the material obtained by treatment with hydroxylamine gave the correct amount of nitrogen for the penta-oxime of leuconic acid, since he was unable to obtain this compound in a crystalline condition, and therefore could not be sure that he was dealing with a pure compound.

On the other hand, Maquenne's assumption of the presence of tetrahydroxyquinone and rhodizonic acid in the oxidation product on the basis of the analysis of the extraordinarily unstable triquinoyl, and of the red color of the salt produced by barium chloride, seemed hardly sufficient proof for the presence of these materials.

Because of the obviously contradictory results of these two investigators,

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[2] Contardi, *Gazz. chim. ital.*, 51, I, 107–125 (1921).

as well as the seemingly rather doubtful basis upon which they interpreted some of their results, it seemed worth while to repeat the work on the oxidation of inosite with nitric acid.

Experimental Part

The inosite was prepared from phytin according to the method used by Contardi.[2] The phytin was obtained from the Corn Products Co. We obtained from this material a nicely crystalline product melting at 218°*, which exhibited all of the properties assigned in the literature to inactive inosite.

Following Contardi's directions, 50 g. of inosite was dissolved in 150 g. of nitric acid (Baker's c. p. fuming, sp. gr. 1.50), and the solution was heated on the water-bath. The reaction soon became rather violent, and large amounts of the oxides of nitrogen were given off. After some time the reaction slowed down somewhat, and the solution was evaporated to dryness. As the residue approached dryness it appeared as a greenish-white sticky mass, but on remaining on the boiling water-bath it soon changed to a light brown color. The material was extremely soluble in water, and effervesced somewhat when placed in solution. It was slightly soluble in alcohol, but insoluble in ether. It showed a very slight trace of oxalic acid.

The residue was now taken up in water and again evaporated on the water-bath. The solution began to turn brown almost immediately, and a slow but steady evolution of carbon dioxide was noted during the evaporation. After some time a brown colored precipitate began to separate, and on evaporating the solution completely to dryness, the residue was almost black, appearing much like carbon. This material was very soluble in water, giving deep brown solutions. No crystalline product was obtained from it. Cold, concentrated nitric acid decolorized it immediately, but the residue which had been decolorized in this way again turned brown when its water solution was evaporated.

The oxidation was repeated in the same way, with the exception that the temperature, neither during the reaction nor during the subsequent evaporation, was allowed to rise above 60°. When the nitric acid solution had evaporated to a thin sirup, it was removed from the water-bath and allowed to cool. Nicely crystalline colorless needles soon separated. These were filtered off with suction, washed with a mixture of half alcohol and half ether, and kept in a vacuum desiccator which contained both concentrated sulfuric acid and solid potassium hydroxide, until they no longer gave a test for nitric acid. The mother liquor from which these crystals had been obtained was concentrated somewhat, and again allowed to cool. Again needle crystals separated. These were purified in the same manner as the previously obtained fraction. In a similar manner a third fraction of crystals was obtained from the mother liquor. These fractions were analyzed separately, and the results of analysis were found to differ quite widely with the different fractions. It was apparent from these results that the three fractions were not made up of a single compound, but of a mixture. The crystalline material was unstable at temperatures around 60°. Its water solutions turned brown with the evolution of carbon dioxide when they were warmed on the water-bath.

An attempt was made to prepare the penta-oxime according to Contardi's directions.2 A small amount of a brown amorphous material was obtained, which exploded at 170° as Contardi's oxime had done. It dissolved in alkali and was reprecipitated on addition of acid, but still in an amorphous condition. Since this material was obtained in very small amounts, and since no method of determining its purity was found, it was not investigated further.

When a solution of the material obtained by the oxidation of inosite was treated with barium chloride solution, the mixture at first became turbid; then a bright red amorphous precipitate settled out. It was upon the result of this reaction that Maquenne based his conclusion that rhodizonic acid was present in the product obtained by the oxidation of inosite with nitric acid. Since this compound could not be obtained crystalline, investigation of the substance was dropped.

Since it seemed apparent that the material obtained by oxidation in this manner was doubtless a mixture of products, we now attempted to carry out a separation of these compounds by converting them into their salts.

Isolation of the Di-potassium Salt of Croconic Acid.—A water solution of the material obtained from the oxidation of inosite with nitric acid in the manner described above, was treated with solid potassium carbonate until the solution showed an alkaline reaction. Immediately upon introduction of the carbonate the solution turned yellow and there was slight effervescence. A bright yellow precipitate soon began to settle out, and by the time the solution was neutral it had become practically solid, due to the large amount of this precipitate. More water was added, but since the material did not seem to go readily into solution, it was warmed slightly. It soon began to effervesce—the precipitate meantime going into solution, and the solution itself took on a dark brown color. It was filtered while warm and allowed to cool, whereupon a small quantity of beautiful violet colored crystals separated. This material was filtered off, and the solution was concentrated to a small volume, and again allowed to cool. A large amount of orange colored needle crystals then settled out. This material was moderately soluble in water, from which it could be easily crystallized. . After several recrystallizations from water the orange crystals were dried in a water jacketed oven at **100°**. On drying, the material became bright yellow in color, but upon recrystallization from water the orange needles were again obtained.

The properties of this compound agreed with those given in the literature for the di-potassium salt of croconic acid. Gmelin[3] had obtained it by the evaporation in air of a water solution of potassium carbonyl. Nietzki and Benckiser[4] obtained it from hexahydroxybenzene by evaporating a water solution of this material in the air, in the presence of potassium hydroxide. The same investigators obtained it in the same manner by evaporating a water solution of either triquinoyl, tetrahydroxyquinone or rhodizonic acid in the presence of potassium hydroxide. Their description applied in every respect to the compound which we had isolated. Consequently we proceeded to analyze the yellow salt.

Anal. Calcd. for $C_5O_5K_2$: C, **27.52;** H, none; **K, 35.77.** Found: ***C*, 27.31, 27.45; H, 0.18, 0.12; K, 35.7, 35 7.**

There remained, therefore, little doubt but that this yellow salt was the di-potassium salt of croconic acid. Since it had been obtained by previous investigators by the evaporation of alkaline solutions of hexahydroxybenzene, tetrahydroxyquinone, rhodizonic acid and triquinoyl, it seemed possible that some of these might have been present in the original material from which potassium croconate had been obtained.

An Attempt to Isolate the Salt of Rhodizonic Acid and the Subsequent Isolation of the Di-sodium Salt of Tetrahydroxyquinone.—As already pointed out, we had obtained a violet crystalline material upon the first treatment of the oxidation product with potassium carbonate. The di-potassium salt of rhodizonic acid was obtained by several investigators[4,5]

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[3] Gmelin, *Ann. phys.*, 4, **31 (1800).**

[4] Nietzki and Benckiser, **Ber., 18, 499–515 (1885);** *ibid.*, **19, 293 (1886).**

[5] Heller, *Ann.*, **34,** 232–235 **(1840);** Will, *ibid.*, **118, 187–206 (1861);** Lerch, *ibid.*, *124*, **20–42 (1862).**

and is described as a violet colored, needle crystalline material that dissolves in water to give orange colored solutions, which yield potassium croconate on evaporation. It therefore seemed probable that the violet material might be the di-potassium salt of rhodizonic acid. However, the yield of this material in the previously described treatment had been very small, and upon repeating the procedure we were seldom able to obtain any of the violet crystals. Some material usually separated, but it was not crystalline, and ranged in color from black to green, with sometimes a small amount of violet.

Since rhodizonic acid in alkaline solutions tends to change over to the salt of croconic acid, it was thought that perhaps the normal carbonate produced too alkaline a medium for the separation of the rhodizonic acid salt, if present. A solution of the oxidized material was therefore treated with solid sodium bicarbonate in small portions. It immediately turned yellow, and there was some effervescence, which continued for some time after each addition. When the solution no longer effervesced upon further addition of the bicarbonate, it was set aside and allowed to stand for some time. Soon a solid began to separate which, on filtering off, was found to be nicely crystalline, but green in color. The same green compound was obtained when sodium acetate, disodium hydrogen phosphate or trisodium phosphate was used in place of the bicarbonate, although the bicarbonate seemed to give the best results. Sodium chloride and sodium sulfate produced none of the green salt.

This green material, like the violet, could not be recrystallized from water, but, dissolved in that solvent, gave the same orange colored solution as the latter, and upon evaporation of the solution only the croconic acid salt was obtained.

Potassium bicarbonate worked in the same way as sodium bicarbonate, giving a material of a slightly darker green color, but not quite so nicely crystalline as the product obtained by the sodium bicarbonate treatment.

In no case under this treatment was there any indication of the production of the violet salt. However Nietzki and Benckiser[4] describe the di-sodium salt of tetrahydroxyquinone as a dark green, crystalline material, which dissolves in water to give an orange colored solution that yields sodium croconate on evaporation. We therefore believed this green material which we had obtained to be the di-sodium salt of tetrahydroxyquinone. Analysis of the compound bore out this supposition.

Anal. Calcd. for $C_6O_6H_2Na_2$: C, 33.3; H, 0.92; Na, 21.3. Found: C, 33.28, 33.76, 32.80, 32.88; H, 1.20, 1.32, 0.98; Na, 21.3, 21.3, 21.0, 21.3.

The slight variation in results may be considered as due to the fact that this compound could not be purified beyond the condition in which it separated from the original solution.

From the results of this analysis, and because of the agreement between the properties of the compound with those given in the literature for the di-sodium salt of tetrahydroxyquinone, we concluded that this green substance must be the di-sodium salt of tetrahydroxyquinone.

Isolation of the Di-potassium Salt of Rhodizonic Acid.—Since the method of procedure just described had not given a method for obtaining the violet material, we now returned to the original treatment with potassium carbonate, in the hope that by suitable adjustment of conditions we might be able to obtain the violet material consistently. After a large number of attempts we were able finally to produce the violet salt at will by the following procedure.

Inosite was oxidized with three times its weight of nitric acid, in the manner formerly described; 25 g. of the product obtained by this oxidation was dissolved in 50 cc of water. When 2 cc. of this solution in a test-tube was treated with 3 cc. of 20% solution of potassium carbonate, the mixture became almost solid, the solid being about the color of ocher. The test-tube and contents were now placed in a beaker of water at a temperature of about 60°. Effervescence began almost immediately, the yellow precipitate began to go into solution, and the solution itself took on a much darker brown color. After about three minutes, the test-tube and contents were removed from the water. Effervescence continued for some time and when this came to an end, all of the yellow precipitate had gone into solution. The solution was dark brown in color When it had cooled a layer of violet crystals about a centimeter deep was found on the bottom of the test-tube.

If the oxidation is carried out with different proportions of nitric acid than given, a new set of conditions for the treatment with potassium carbonate must be determined. The amount of the violet salt obtained does not appear to vary appreciably when the amount of nitric acid is varied over moderate limits.

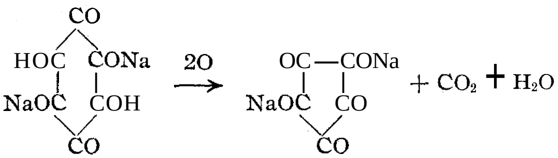
Analysis of the violet salt confirmed our belief that the violet salt was the di-potassium salt of rhodizonic acid.

Anal. Calcd. for $C_6O_6K_2$: C, 29.67; H, none; K, 31.6. Found: C, 29.15, 29 29, 29.66, 29.73, 29.40; H, 0.04, 0.16, 0.01, 0.18, 0.12; K, 31.1, 31.8, 31.2, 31.5, 31.2.

Quantitative Conversion of Six-Membered Ring Compounds to Compounds Having Five-Membered Rings.—Although it appeared certain from the results obtained thus far that some of the products in the oxidation of inosite with nitric acid were six-membered ring compounds, we deemed it advisable to try another method of investigation in order to give further proof of this fact.

As already pointed out, other investigators have shown that the salts of both rhodizonic acid and tetrahydroxyquinone in water solution change over to the corresponding salts of croconic add. We have also pointed out that the compounds we obtained exhibited the same phenomenon. The reactions involved in this transformation would be represented as follows

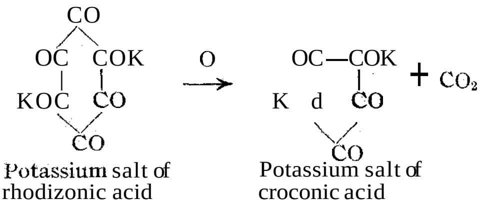
I



Sodium salt of tetra-oxyquinone

Sodium salt of croconic acid

II



Upon consideration of these equations it will be seen that they should lend themselves to a fairly simple quantitative investigation. Indeed they have the advantage that they offer three different ways in which the course of the reaction can be checked quantitatively. Taking Reaction I as an example, in the first place the amount of carbon dioxide can be absorbed and weighed. The weight of the carbon dioxide obtained should correspond to one molecule for every molecule of the di-sodium salt of tetrahydroxyquinone employed. In the second place, if the reaction takes place quantitatively according to the above equation, the weight of the tetrahydroxyquinone salt employed in the determination should be to the weight of the residue after the reaction has taken place, as the molecular weight of the di-sodium salt of tetrahydroxyquinone is to the molecular weight of the di-sodium salt of croconic acid. Finally, the amount of sodium in the residue obtained after the reaction has taken place, should correspond to the percentage of sodium in sodium croconate, while the amount present in the original material corresponds to that in the di-sodium salt of tetrahydroxyquinone.

The second reaction can lend itself to the same sort of quantitative determination, likewise offering three ways in which to obtain a quantitative check on the conversion.

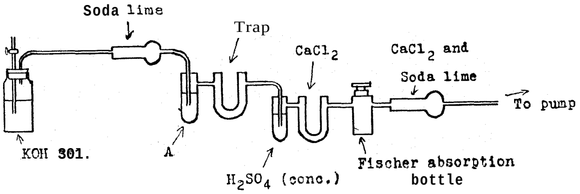


Fig. 1.—Diagram of apparatus.

In order to carry out these reactions the apparatus shown in Fig. 1 was constructed. Tube **A** was first filled about two-thirds full of distilled water, and was then surrounded by a beaker of water kept at about 80°. Air that had been purified from carbon dioxide by passing through the purification train shown was drawn slowly through the whole apparatus by means of a suction pump. The Fischer absorption bulb was taken off from time to time and weighed. When it no longer increased in weight, the apparatus was ready for use. Accordingly, a weighed sample of the green salt was introduced into the water in tube **A**, and air was drawn through the resulting solution until the absorption bulb no longer gained in weight. This required about three hours. The total increase in weight of the absorption bulb corresponded to the amount of carbon dioxide lost by the sample of the di-sodium salt of tetrahydroxyquinone in changing to the di-sodium salt of croconic acid. The solution remaining in tube A was transferred to a weighed platinum crucible and evaporated to constant weight. The difference between the weight of the original sample and the weight of the residue thus obtained corresponded to the loss in weight that the original sample of the di-sodium salt of tetrahydroxyquinone should undergo in changing to the di-sodium salt of croconic acid. The residue in the crucible was now ashed, dissolved in water and finally titrated with standard hydrochloric acid, using methyl orange as indicator, the percentage of sodium present in the residue being then calculated as the carbonate. The amount of sodium present in the residue was found to correspond to the correct percentage of the residue obtained by the evaporation of the water solution, if that residue were pure sodium croconate.

The violet salt was subjected to similar treatment, and the results were found to agree exceptionally well with the results expected if the di-potassium salt of rhodizonic acid changed quantitatively to the di-potassium salt of croconic acid, according to Equation II above. The results of the analyses are given in Tables I and II. Table I is the result of the treatment of the green salt, while Table II represents the analysis of the violet material.

TABLE I

ANALYSIS OF GREEN SALT

Sample, g.	CO_2 found, g.	CO_2 calcd., g.	Residue found, g.	Residue calcd., g.	Na found, calcd on residue obtained, %	Na calcd. for $Na_2C_5O_5$, %
0.1216	0.0243	0.0247	0.1008	0.1047	24.1	24.7
.0930	.0188	.0189	.0725	.0800	24.5	

TABLE II

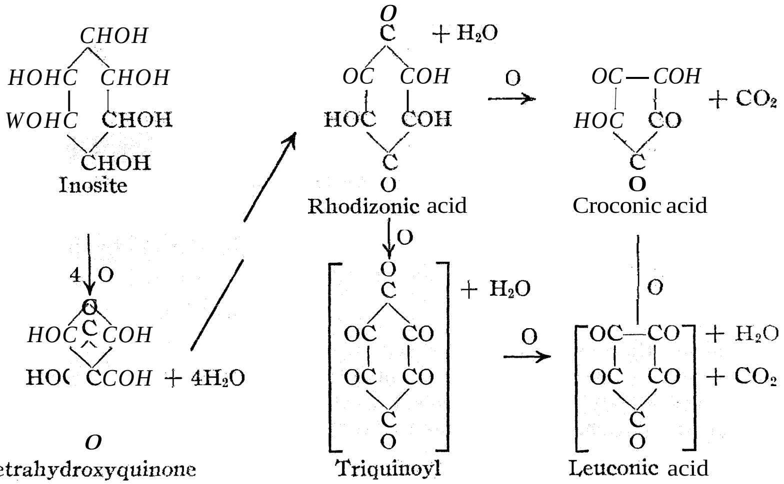
ANALYSIS OF VIOLET MATERIAL

Sample, g.	CO_2 found, g.	CO_2 calcd., g.	Residue found, g.	Residue calcd., g.	K found. calcd. on residue obtained, %	K calcd. for $K_2C_5O_5$, %
0.0987	0.0180	0.0175	0.0866	0.0867	35.4	35.7
.0902	...	...	.0846	.0843	35.3	
.1104	.0203	.0197	.0982	.0978	35.7	

(No result was obtained for the carbon dioxide in the second sample in Table II, due to the fact that a leak developed in the apparatus during this run.)

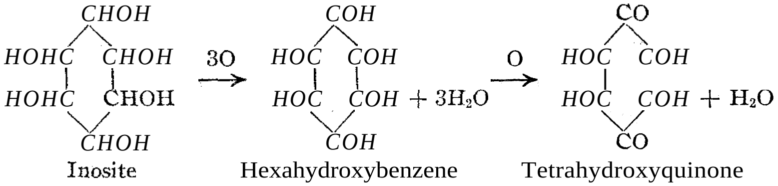
From the results thus obtained there can no longer be any doubt that six-membered products are obtained in the oxidation of inosite with nitric acid, and we can represent the reaction on the basis of the results obtained on the following page.

While direct derivatives of the products indicated in brackets (triquinoyl and leuconic acid) have not been isolated by us, we believe that it is highly probable that they are formed in the course of the reaction, since Nietzki and Benckiser[4] have shown that triquinoyl is easily produced from tetrahydroxyquinone or rhodizonic acid by oxidation with nitric acid, and Will[5] obtained leuconic acid by the oxidation of croconic acid with nitric acid. All of these are so unstable in the free condition that we feel more justified in concluding their presence on the basis of the much more stable salts



which we isolated than on the grounds of the analysis of the free compounds. At any rate, we can certainly conclude that tetrahydroxyquinone, rhodizonic acid, and croconic acid may be numbered among the compounds obtained by the oxidation of inosite with nitric acid.

Possibility of Hexahydroxybenzene as an Oxidation Product of Inosite.—On inspection of the reactions given above it will be seen that the successive reactions take place in quite an orderly manner, and that they proceed for the most part by the removal of two hydrogens from the first compound to give the second. Thus tetrahydroxyquinone is converted into rhodizonic acid by the removal of two hydrogens by oxidation. It, therefore, seemed logical that the tetrahydroxyquinone found in the mixture of oxidation products might have originated by a similar reaction from hexahydroxybenzene, which could have been formed in the reaction as follows



Indeed Lerch[6] as well as Nietzki and Benckiser[4] had obtained tetrahydroxyquinone, rhodizonic acid and triquinoyl by the oxidation of hexahydroxybenzene with nitric acid. We therefore set out to ascertain, if possible, whether hexahydroxybenzene was contained in the mixture of products which we had obtained by the oxidation of inosite.

Isolation of Hexahydroxybenzene Hexa-acetate.—Hexahydroxybenzene had been identified by Nietzki and Benckiser,[4] who first prepared the

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[6] Lerch, *Ann.*, 124, 20–41 (1862).

compound, by the fact that upon acetylation with acetic anhydride in the presence of sodium acetate they were able to isolate a crystalline substance which showed the correct composition for the hexa-acetate of hexahydroxybenzene. This material they describe as very insoluble in most reagents, but crystallizable from boiling glacial acetic acid, in which it is slightly soluble. The material separated in colorless microscopic cubes which contained acetic acid of crystallization; this was driven off by heating at 150°. The compound melted sharply at 203°. The original material before acetylation also yielded benzene and diphenyl when distilled with zinc dust.

We believed that if hexahydroxybenzene were one of the products of oxidation, we might be able to identify it through acetylation after the method of Nietzki and Benckiser. Accordingly, **5** g. of the product obtained by the oxidation of inosite in the manner originally described, was refluxed for one hour with **100** cc. of acetic anhydride in the presence of **3** g. of fused sodium acetate. During the heating the reaction mixture became dark brown in color. It was allowed to cool and then poured into about **200** cc. of cold water. A precipitate separated, which was filtered off, washed with hot water for some time, then with hot alcohol, and finally with ether. The material remaining was of a light tan color, and was extremely insoluble in practically all ordinary solvents. It dissolved with some difficulty in boiling glacial acetic acid, from which it crystallized very quickly on slight cooling. The material obtained in this way appeared under the microscope to be made up of very small but well-formed almost colorless cubes. After several recrystallizations from glacial acetic acid the material was entirely colorless and melted sharply at 204°. It contained acetic acid of crystallization as had the compound obtained by Nietzki and Benckiser. However, after heating at 150° for some time, the weight became constant, and the material was subjected to analysis.

Anal. Calcd. for $C_6(OOCCH_3)_6$: C, **50.72;** H, **4.22.** Found: **C, 50.48, 50.43;** H, **4.43, 4.30.**

From these results hexahydroxybenzene may be considered as one of the products obtained in the oxidation of inosite with nitric acid.

In order to ascertain the conditions of oxidation that were favorable to the maximum production of hexahydroxybenzene, a series of oxidations was run, using different amounts of nitric acid, and acetylating the entire oxidized product. By the amount of product obtained in the latter reaction, a relationship between the amounts of hexahydroxybenezene that were produced by varying proportions of nitric acid was obtained. The results of the treatment are given in Table III. The weight of acetylated product given is that of the crude product after being washed with hot water, hot alcohol and ether. This weight was taken, rather than the weight of the product after recrystallization from glacial acetic acid, since a considerable amount of material was always lost during this treatment, due to the tendency of the material to adhere to the crystallizing vessel.

It thus appears that the maximum amount of hexahydroxybenzene is produced when inosite and nitric acid are employed in the proportion of 5 g. of the former to 6 cc. or **9** g. of the latter. Where very small amounts

TABLE III

EXPERIMENTAL DATA

Inosite, g.	Nitric acid, cc.	Acetylated product, g.	Inosite, g.	Nitric acid, cc.	Acetylated product, g.
5	2.5	1.36	5	6.0	1.90
5	2.5	1.24	5	7.0	1.56
5	4.0	1.71	5	7.0	1.48
5	4.0	1.81	5	10.0	1.24
5	5.0	1.78	5	10.0	1.45
5	5.0	1.89	5	25.0	0.72
5	6.0	2.16	5	25.0	0.76

of nitric acid were used some inosite hexa-acetate was obtained, showing that some of the inosite originally present had not been attacked by the nitric acid.

Although from the results of previous investigators the structure of the numerous compounds which we have encountered in this investigation (hexahydroxybenzene, tetrahydroxyquinone, rhodizonic acid, etc.) seemed to be reasonably well established, in no case has a molecular weight determination been reported on any of these compounds or their derivatives. It was hoped that we might be able to give further proof of the correctness of the proposed formulas by obtaining the molecular weights of some of the derivatives that we had isolated.

Attempts to obtain the molecular weight of potassium croconate by the freezing point depression method, using water as solvent, were unsuccessful because of the high degree of dissociation of this salt in water. Attempts to obtain the molecular weight of hexahydroxybenzene hexa-acetate by the boiling point elevation method, using glacial acetic acid as solvent, and by the freezing point depression method, using nitrobenzene as solvent, were unsuccessful because of the extremely slight solubility of the compound in these solvents.

We were likewise unsuccessful in attempts to obtain methyl ethers. Attempts were made to obtain them in the hope that they might lend themselves to a determination of molecular weight. The potassium salt of croconic acid was treated with methyl sulfate and silver croconate was subjected to the action of methyl iodide, but the only evidence of methylation was a very small amount of an ether-soluble oil. The complete oxidation product was also subjected to the action of diazomethane, but here again only a very small amount of ether-soluble oil gave any indication that methylation had taken place. Attempts to methylate inosite itself by means of diazomethane were also unsuccessful.

Conclusions

From the results obtained in this investigation it is obvious that in oxidizing inosite with nitric acid, a large number of products are obtained.

It is also obvious that the apparent contradiction pointed out in the literature is due to the fact that the two investigators did not succeed in isolating a sufficient number of products from the resulting mixture to establish all the intermediate steps in the progressive course of the reaction.

From the results given above, we then conclude that the products obtained in the oxidation of inosite with nitric acid, in the order formed, are hexahydroxybenzene, tetrahydroxyquinone, rhodizonic acid, croconic acid and triquinoyl, and finally leuconic acid. While neither triquinoyl nor leuconic acid has been isolated in this investigation, we include them among the products for reasons given in the text.

SYRACUSE, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

SYNTHESIS OF THE POLYPEPTIDE-HYDANTOIN, N-3-METHYL-5-TYROSYL-HYDANTOIN-1-PHENYLACETIC ACID

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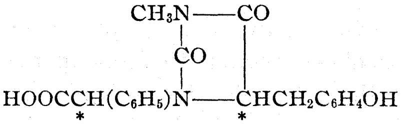
The present investigation was undertaken with a view to extending the knowledge of polypeptide-hydantoins. The particular combination was chosen in order to confirm if possible a previous observation[2] that the presence of two asymmetric carbon atoms in the polypeptide-hydantoin molecule is associated with isomerism of the meso and racemic type and at the same time to continue a study of the effect of substitutions in the N-1-position upon the mobility of the molecule as shown in its tendency to isomerize and also to split off groups in the N-1-[3] and in the C-5- position^.^

With these ends in view the following substance was selected for synthesis, the asymmetric carbon atoms being indicated by asterisks.[5]



$$\begin{array}{rcl} & CH_3N\text{——} & CO \\ & | & | \\ & CO & | \\ & | & | \\ HOOC\underset{*}{C}H(C_6H_5) & N\text{——} & \underset{*}{C}HCH_2C_6H_4OH \end{array}$$

A substance of the above configuration has further interest in that it may be expected to add two molecules of water on hydrolysis to give the N-phenylacetic acid derivative of tyrosine

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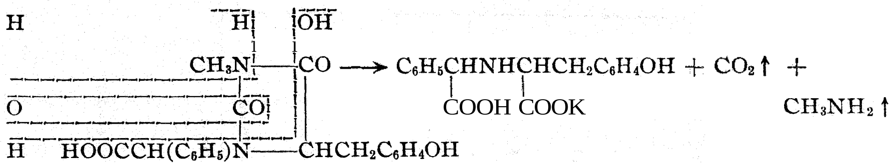
[1] This work was offered in partial fulfilment of the requirements for the degree of Master of Arts at Mount Holyoke College.

[2] Hahn and Gilman, THIS JOURNAL, 47, 2944 (1925).

[3] Hahn and Kenfrew, *ibid.*, 47, 156 (1925).

[4] Hahn and Evans, *ibid.*, 49,2878 (1927) and 50,810 (1928).

[5] The system of numbering the positions of the atoms in the hydantoin ring has been changed from that used in previous papers to the one now in use by T. B. Johnson, cf. *ibid.*, 51, 255 (1929), and in the subject index of *Chemical Abstracts*.



$$\begin{array}{l} H \quad\quad\quad \overset{H\,OH}{CH_3N{-}CO} \\ O \quad\quad\quad CO \\ H \quad HOOCCH(C_6H_5)N{-}CHCH_2C_6H_4OH \end{array} \longrightarrow C_6H_5\underset{COOH}{CH}NH\underset{COOK}{CH}CH_2C_6H_4OH + CO_2\uparrow + CH_3NH_2\uparrow$$

and the fact that polypeptide-hydantoins of this type decompose in this way affords an excellent and clear method for preparing imino dibasic acids which contain aromatic residues.[6]

The synthesis of N-3-methyl-5-tyrosylhydantoin-N-1-phenylacetic acid was accomplished by means of a series of reactions which are indicated by arrows on the accompanying chart. The latter is somewhat complicated because of the fact that all of the intermediate compounds exist in two or more isomeric modifications. The primary reaction consisted in condensing the sodium derivative of N-3-methyl-5-anisalhydantoin with ethyl phenylbromo-acetate. The principal product consisted of the more stable modification of ethyl N-3-methyl-5-anisalhydantoin-N-1-phenylacetate, I, in yields averaging 74% of the theoretical, while small quantities of a labile form, II, were separated from the filtrates. Of these the former was employed in all subsequent major operations while the latter was used only where necessary in establishing the various chemical relationships. The principal transformations by means of which the polypeptide-hydantoin XXI was obtained consisted in reduction (to XI and XII), saponification (to the acids XV to XIX) and finally demethylation in the presence of hydrogen iodide.

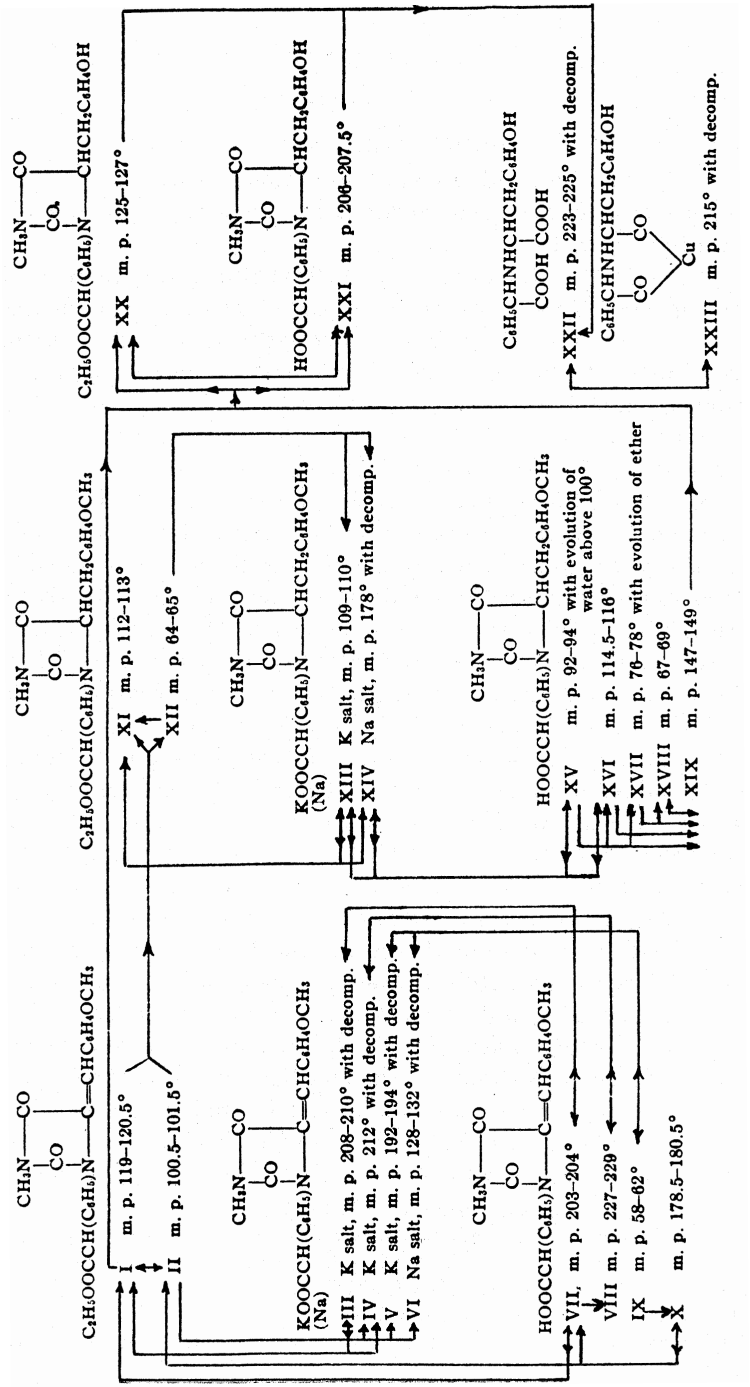
The constitutional formulas given in the chart are supported not only by evidence obtained from a study of the chemical relationships of the various substances, but by the fact that a corresponding relationship in their physical properties has been established as the result of spectrographic analyses.[7] In this connection it is interesting to note that the absorption curves plotted for the esters I and II are almost identical with those previously obtained in the case of the geometrically isomeric modifications of N-1-methyl-5-benzalhydantoin-N-3-acetic acid,[8] a fact which must be construed as furnishing additional evidence in support of the configuration of the former substances and of their derivatives. Still further confirmation of these formulas is shown by the fact that the polypeptide-hydantoin XXI decomposes to give methylamine and the imino dibasic acid XXII, the latter having been identified by means of analyses both of the free acid[9] and its corresponding copper salt.

[6] Hahn and Renfrew, THIS JOURNAL, 47, 148 (1925).

[7] A full discussion of the data has been reserved for a second paper, "The Isomerism of Certain Acids Obtained in the Synthesis of N-3-methyl-5-tyrosylhydantoin-N-1-phenylacetic Acid," *ibid.*, 52, 2505 (1930).

[8] Hahn and Evans, ibid., 50, 808, 809, 810 (1928).

[9] Other derivatives of this acid have been prepared and will be reported upon later.


CH3N—CO
CO
C2H5OOCCH(C6H5)N—C=CHC6H4OCH3
I m. p. 119–120.5°
II m. p. 100.5–101.5°
KOOCCH(C6H5)N—C=CHC6H4OCH3
(Na)
III K salt, m. p. 208–210° with decomp.
IV K salt, m. p. 212° with decomp.
V K salt, m. p. 192–194° with decomp.
VI Na salt, m. p. 128–132° with decomp.
HOOCCH(C6H5)N—C=CHC6H4OCH3
VII m. p. 203–204°
VIII m. p. 227–229°
IX m. p. 58–62°
X m. p. 178.5–180.5°
C2H5OOCCH(C6H5)N—CHCH2C6H4OCH3
XI m. p. 112–113°
XII m. p. 64–65°
KOOCCH(C6H5)N—CHCH2C6H4OCH3
(Na)
XIII K salt, m. p. 109–110°
XIV Na salt, m. p. 178° with decomp.
HOOCCH(C6H5)N—CHCH2C6H4OCH3
XV m. p. 92–94° with evolution of water above 100°
XVI m. p. 114.5–116°
XVII m. p. 76–78° with evolution of ether
XVIII m. p. 67–69°
XIX m. p. 147–149°
C2H5OOCCH(C6H5)N—CHCH2C6H4OH
XX m. p. 125–127°
HOOCCH(C6H5)N—CHCH2C6H4OH
XXI m. p. 206–207.5°
C6H5CHNHCHCH2C6H4OH
COOH COOH
XXII m. p. 223–225° with decomp.
C6H5CHNHCHCH2C6H4OH
CO CO
Cu
XXIII m. p. 215° with decomp.

In conclusion emphasis must be given to the fact that the substitution of phenyl for hydrogen in the acetic acid group in the N-1-position has been observed greatly to increase the mobility of the molecule.[10] This is shown by the facts (a) that a greater number of isomers has been obtained than would ordinarily be expected in the case of both the saturated and unsaturated molecules of a given configuration, (b) that certain of these compounds show a marked tendency to associate water or ether molecules (*i.* e., the acids XV and XVII), (c) that the rate of isomerization of the labile to the stable modifications is very rapid[11] and finally (d) that the unsaturated esters I and II show an increased disposition under the action of alkali to split off either the acid group in the N-1-position[12] or the aldehyde group in the C-5-position.

The existence in certain cases of a number of isomeric modifications greater than was to be expected on the basis of geometrical[13] or stereo-[14] isomerism offers difficulties in the way of interpretation. Of these the unsaturated acids have been set apart for discussion in a separate paper.' The saturated isomers may be explained by assuming that XVI and XIX represent stereoisomeric inactive forms and that XVIII is a desmotropic modification[15] of the latter.

Experimental

Ethyl-N-3-methyl-5-anisalhydantoin-1-phenylacetate, I, m. p. 119–120.5°,[16] was prepared by alkylating the sodium derivative of N-3-methyl-5-anisalhydantoin with or-phenyl-or-bromo-acetic ester. The latter was purchased from Kahlbaum while the N-3-methyl-5-anisalhydantoin was prepared in the usual way.[17] The following procedure was found to give the best percentage yields.

Fifty grams of N-3-methyl-anisalhydantoin, m. p. 212–215°, was suspended in 300 cc. of 95% ethyl alcohol to which 1.2 equivalents of sodium had been added. The mixture was shaken vigorously to prevent caking of the methyl-anisalhydantoin, which did not dissolve, but was held in suspension during the process of conversion into the corresponding sodium derivative which was also insoluble. After boiling with a reflux condenser for one and one-half to two hours, 1.2 equivalents of ethyl phenyl-bromoacetate was added along with 100 cc. of alcohol used for rinsing. Within twenty minutes after the addition of this material a vigorous bubbling took place, which was accompanied

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[10] Compare the behavior of these substances with the corresponding derivatives of ethyl N-3-methyl-5-anisalhydantoin-N-1-acetate, Hahn and Renfrew, THIS JOURNAL, **47, 147** (1925).

[11] XII isomerizes so rapidly that substantial losses are suffered in one recrystallization from alcohol.

[12] Compare Hahn and Renfrew and Hand and Evans, THIS JOURNAL, **47,** 156 (1925); 50, 811 (1928).

[13] Compare the unsaturated acids **VII** to **X** on the chart.

[14] Compare the saturated acids **XVI, XVIII** and **XIX** on the chart.

[15] The equilibrium **XVIII** $\rightleftarrows$ XIX *represents* a thermal relationship, one acid existing only at relatively high and the other at ordinary temperatures.

[16] This substance was first prepared by Miss Marie A. Dobbrow.

[17] (a) Johnson and Nicolet, *Am. Chem.* J., **47,** 469 (1912); (b) Hahn and Renfrew, THIS JOURNAL, **47,** 156 (1925).

by the solution of the yellow sodium derivative and the precipitation of a fine white powder. In the preliminary experiments the latter was filtered hot and identified as a mixture of methyl-anisalhydantoin and sodium bromide. Ordinarily no separation was attempted at this point, but the boiling was continued for about two hours or until the solution became neutral to turmeric. On cooling a heavy white precipitate was formed which melted between 110 and 200°. This was filtered and when dry extracted with 100 cc. of cold chloroform in order to separate the reaction product from any unchanged methyl-anisalhydantoin and sodium bromide. The extract was evaporated to small volume in order to remove the chloroform and 200 cc. of hot alcohol was added. On cooling, 34 g. of the ester, m. p. 116–118°, crystallized out. The residue, insoluble in chloroform, yielded 23 g. of methyl-anisalhydantoin, m. p. 212–214°, along with varying quantities of sodium bromide.

This amount of reaction product (averaging about 74% as calculated on the basis of the methyl-anisalhydantoin which reacted) remained practically constant even when the period of the reaction was extended from two and one-half to fifty-two hours, but was decreased if the heating was continued for a longer time. In cases where the heating was continued for five days the product consisted of an oil from which it was impossible to separate any solid product.

The crude ester was readily purified by recrystallization from alcohol, from which it separates in the form of white silky rosets which fill the entire solution, m. p. 119–120.5". One gram dissolves in 3.5 cc. of boiling alcohol, and in 70 cc. of cold alcohol.

Anal. Calcd. for $C_{22}H_{22}O_5N_2$: N, 7.10. Found: N, 7.14, 7.04.

The ester was partly transformed into the lower-melting isomer II by saturating its alcohol solution with hydrogen chloride gas. On alkaline hydrolysis the ester I was changed into a mixture of the potassium salts III and IV. The latter when separated and acidified in aqueous solution gave the acids VII and VIII, respectively. Acid hydrolysis resulted in the formation of the acid III alone. Reduction of the ester I to the isomeric saturated esters XI and XII took place readily under the action of hydrogen in the presence of palladium. By treatment of the ester with hydrogen iodide the demethylated saturated acid XXI was formed.

Ethyl-N-3-methyl-5-anisalhydantoin-1-phenylacetate, II, m. p. 100.5–101.5°, was obtained by the action of dry hydrogen chloride gas on an alcohol solution of the higher-melting isomer, I.

Forty grams of the ester, m. p. 119–120.5°, was dissolved in a mixture of 300 cc. of 95% alcohol and 150 cc. of cold chloroform. During a period of twenty-five to thirty hours the solution was alternately saturated with hydrogen chloride and heated for one hour on a water-bath. The product of the reaction consisted of a hard gum which would not crystallize in the presence of even small quantities of hydrogen chloride. It was, therefore, taken up in chloroform and washed free from acid. The chloroform extract was dried, concentrated to small volume, diluted with alcohol to bring the volume to 600 cc., and cooled, when 10 g. of hard, pale yellow needles, m. p. 96–100°, separated. After two recrystallizations from boiling alcohol a pure substance of m. p. 100.5–101.5° was obtained. The filtrates from this substance (which contained the remainder of the original 40 g. of ester I) when concentrated and treated again with hydrogen chloride gave additional amounts of the lower-melting isomer in about the same ratio as before, *i.* e., approximately 1:4. No loss of material was involved in this procedure, since after washing free from hydrogen chloride the mixture of the two esters could be separated mechanically. The higher-melting modification crystallized from alcohol in the form of white, fluffy needles and could be readily floated off with alcohol from the heavy compact crystals which formed on the bottom of the beaker and which represented the lower-melting isomer.

Anal. Calcd. for $C_{22}H_{22}O_5N_2$: N, 7.10. Found N, 6.92, 6.93.

The lower-melting ester, II, was transformed into the higher-melting ester I by the action of sunlight on its ether solution. Five-tenths of a gram of ester, m. p. 100.5–101.5°, was dissolved in 250 cc. of dry ether and allowed to stand in the sunlight in a glass bottle for three and one-half months. After evaporation of the ether a gummy product was obtained which on treatment with alcohol yielded 0.1 g. of ester, m. p. 113–118". The crystalline product after one recrystallization from alcohol did not lower the melting point of an analyzed specimen of the ester I, m. p. 119–120.5".

The ester II is very soluble in boiling alcohol (1 g. in 4.4 cc.) and slightly soluble in cold alcohol (1 g. in 70 cc.). It yields on acid hydrolysis two isomeric acids VII and X. On alkaline hydrolysis the corresponding sodium and potassium salts VI and V were obtained which were transformed into the acid IX as primary product and finally into the acid X. By reduction with hydrogen in the presence of palladium the lower-melting ester is changed into the *same* saturated esters, XI and XII, that were obtained from the higher-melting isomer.

Ethyl N-3-methyl-5-anisylhydantoin-1-phenylacetate exists in the form of two isomeric esters: I, m. p. 112–113°, and XI, m. p. 64–65". Both result from the reduction of either of the unsaturated esters I or II with hydrogen in the presence of palladium.[18] For example, twenty grams of the ester, m. p. 112–113°, was dissolved in 250 cc. of 95% alcohol and shaken with 0.6 g. of colloidal palladium (25%) in an atmosphere of hydrogen for two days. For the first hours of this time it was necessary to heat the mixture with steam in order to keep the unsaturated ester in solution, but after a certain amount of hydrogen had been absorbed this was no longer necessary. At the end of the reaction the colloid was precipitated by boiling with 1 cc. of acetic acid and filtered. The filtrate was concentrated to 200 cc. and allowed to cool, when the reduced ester XI separated from the solution in almost pure condition, m. p. 111–112°. A further quantity of the same substance was obtained from the filtrate, making the immediate yield of crystalline product 50% of the theoretical. On recrystallization from alcohol the ester melted at 112–113°.

Anal. Calcd. for $C_{22}H_{24}O_5N_2$: N, 7.07. Found: N, 6.90, 7.04.

The filtrates from the above crystals, on evaporation, yielded an oil which, after standing for several weeks and being periodically agitated with alcohol, gave a series of crystalline precipitates which melted, respectively, at 68–71, 71–100°, etc. The sample having the lowest melting point, when recrystallized from alcohol, finally yielded a new substance, XII, m. p. 64–65°, which was identified as an ester isomeric with XI.

Anal. Calcd. for $C_{22}H_{24}O_5N_2$: N, 7.07. Found: N, 7.07, 7.07.

That the entire product resulting from the reduction of either of the unsaturated esters I or II consisted of the above two isomeric saturated esters was shown by the fact that both the crystalline ester XI and the oil obtained from its filtrates gave the same crystalline sodium salt, XIV, in amounts corresponding almost exactly with the theoretical. A slight amount of decomposition during the process of reduction was evident from the appearance of traces of methyl-anisalhydantoin in the reaction product. Both saturated esters were also obtained by reduction of the unsaturated ester II. Due to the extreme solubility of the latter in alcohol, the reaction could be carried out without heating.

The saturated ester XI is soluble in boiling alcohol (1 g. in 8 cc.) and less soluble in cold alcohol (1 g. in 55 cc.), from which it separates in the form of large transparent

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[18] Acknowledgment is made to Lillian Nelson and Katherine Haring for preparing these esters.

rhombic crystals. The ester may be transformed quantitatively into the potassium salt XIII or sodium salt XIV by alkaline hydrolysis.

The ester XII is extremely unstable and when recrystallized from warm alcohol with even the minimum amount of heating is partially isomerized to the ester XI. For example, 1.8 g. of ester, m. p. 64–65°, when dissolved in 20 cc. of hot alcohol, gave on cooling first 0.5 g. of crystalline precipitate, m. p. 107–109°, and then 0.6 g., m. p. 64–65°. The combined filtrates from these crystals on evaporation gave an oil which crystallized only after long standing and which was found to consist of a mixture of these two isomers. The ester XII was transformed quantitatively into the same potassium and sodium salts, XIII and XIV, that were obtained from its higher-melting isomer.

Potassium N-3-methyl-5-anisylhydantoin-1-phenylacetate, **XIII**, m. p. 109–110°, and sodium N-3-methyl-5-anisylhydantoin-1-phenylacetate, **XIV**, m. p. 178° with decomposition, were both prepared in quantity by saponifying the ester XI. The reactions, which were carried out by boiling in alcohol solution with an equivalent of potassium hydroxide or sodium alcoholate, were complete in ten minutes, and on cooling the salts crystallized in the form of fine white needles. When recrystallized from alcohol the potassium salt separated as large transparent plates which melted at 88–90°. On exposure to the air the crystals rapidly became opaque, lost alcohol of crystallization and the melting point changed to 94–110°. When alcohol-free (after heating in the oven at 80°) the potassium salt melted sharply at 109–110°. The sodium salt when purified by recrystallization from alcohol or water melted with decomposition at 178°.

Anal. Calcd. for $C_{20}H_{19}O_5N_2K$: N, 6.90. Found: N, 6.81, 6.61. Calcd. for $C_{20}H_{19}O_5N_2Na$: N, 7.18. Found: N, 6.85, 6.73.

Both salts when dissolved in cold absolute alcohol and treated with hydrogen chloride passed quantitatively into the ester XI. When acidified in aqueous solution both passed quantitatively into the acids XV or XVI depending on the conditions of the experiment.

N-3-methyl-5-anisylhydantoin-1-phenylacetic Acids.—Five different and well-defined modifications were obtained by the hydrolysis of the potassium or sodium salts, XIII or XIV, respectively, each salt giving one or another of these products depending upon the conditions under which the acid was precipitated and subsequently treated. The relationships between these different substances is shown in the preceding chart.[19]

The acid XV was the primary product usually obtained from the sodium salt XIV or potassium salt XIII. For example, when a cold aqueous solution of either salt was acidified, a gummy mass was precipitated, which on standing, for two hours in the cold solution hardened and disintegrated with the formation of a white powder. This melted at 88–90° and gave off water vapor above 100°. When purified by solution in twice its volume of warm alcohol and precipitated by the addition of an equal volume of water, it melted at 92–94° and began to give off water vapor at about 100°. When heated for one and one-half hours in an oven at 80° it was completely transformed into the anhydrous modification, XVI, melting at 114.5–116°, and suffered a loss in weight corresponding to one molecule of water. The same change took place on standing for several days at room temperature. When recrystallized from concentrated alcohol solutions or from ether, the acid XV passed quantitatively into the stable modification XIX, m. p. 147–149°.

Anal. Calcd. for $C_{20}H_{20}O_5N_2 \cdot H_2O$: N, 7.25. Found: N, 7.10, 7.04.

The acid XVI may be obtained from XV as above, or directly in crystalline form by acidifying an aqueous solution of either the potassium salt XIII or the sodium salt

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[19] Page 2496.

XIV. However, although it was prepared by the latter method in two experiments, the conditions which favored the precipitation of XVI rather than XV could not be determined. When an analyzed specimen of XVI was heated at 87° for twelve hours, it passed quantitatively without loss in weight into the stable isomer XIX. The same transformation was readily effected by recrystallization from ether.

Anal. Calcd. for $C_{20}H_{20}O_5N_2$: N, **7.61.** Found: N, **7.51, 7.40.**

The acid XVII, m. p. 76–78° with evolution of ether, was formed when the gummy acid precipitated from the salt solution was not allowed to stand under water, but was immediately taken up in ether. On evaporation of the ether the acid crystallized in the form of small transparent plates. When a sample of this acid was heated to constant weight, a mole of ether was given off and the acid XIX was formed.

Anal. Calcd. for $C_{20}H_{20}O_5N_2 \cdot (C_2H_5)_2O$: N, **6.34.** Found: N, **6.34, 6.26.**

The acid XVIII, m. p. **67–69',** was formed by fusing at high temperatures either the acid XVII or XIX. When the acid XVII was heated on an oil-bath and the temperature raised slowly to 140° during a period of one and one-half hours, the liquid on cooling solidified as a hard crystalline mass which now melted at **67–69°.** This was ground in a mortar, heated in the oven at 50° to drive off the last traces of ether, and analyzed.

Anal. Calcd. for $C_{20}H_{20}O_5N_2$: N, 7.61. Found: N, **7.63, 7.50.**

The same product was obtained when the acid XIX was held at a temperature of 160–170° for one and one-half hours, and then cooled. **A** sample of the analyzed specimen, m. p. **67-69",** which was kept in the oven at 50° for four weeks showed a gradual rise in melting point to 139–144°, approaching that of the acid XIX. The same change took place more gradually at ordinary temperatures on standing and was brought about quickly by one recrystallization of the substance melting at **67**–69° from ether. Under these conditions it was transformed quantitatively into the acid melting at 147–149°. These experiments were repeated a number of times, so that it would seem reasonable to conclude that the acid XVIII represents a modification which is stable only at higher temperatures and which at ordinary temperatures reverts to a more stable form.

The acid XIX, m. p. 147–149°, represents a modification which is most stable at ordinary temperatures and to which all of the other acids of this series, *viz.*, XV, XVI, XVII and XVIII, revert either on recrystallization or upon long standing. It is most readily purified by crystallization from chloroform–ether mixtures (1:10), from which it separates upon cooling in the form of transparent plates.

Anal. Calcd. for $C_{20}H_{20}O_5N_2$: N, **7.61.** Found: N, **7.68, 7.67.**

The acid neutralizes a theoretical quantity of standard base when titrated in alcohol solution with phenolphthalein as indicator. The acid is transformed into the ester XI in 70% yield when dissolved in alcohol previously saturated with hydrogen chloride and boiled for one hour on the water-bath. The acid is rapidly demethylated when heated with hydrogen iodide and red phosphorus at **a** temperature of 100–110°.

N-3-methyl-5-*p*-hydroxybenzylhydantoin-N-1-phenylacetic Acid, XXI.—Acids corresponding to the above formula exist in the form of at least two and probably more isomers but because of what appears to be a tendency of these substances to isomerize in all solvents, it was never possible to isolate more than one product, namely, XXI, m. p. 206–207.5°, in pure condition. Various reactions all leading to the formation of such isomers were made the subject of intensive study over a period of more than one year and represent (a) demethylation of XIX, (b) saponification and demethylation of XI and (c) reduction, saponification and demethylation of I. In all cases the reaction was brought about by the action of hydrogen iodide in the presence of red phosphorus and in every case the practical results were the same, the product consisting of a mixture of acids partly crystalline and partly oil.

(a) In this case the reaction could bc followed quantitatively by using the Zeisel method and measuring the amount of methyl iodide evolved. For example, 8 g. of N-3-methyl-5-anisylhydantoin-N-1-phenylacetic acid, m. p. 147–149°, when suspended along with 2 g. of red phosphorus in 14 cc. of hydrogen iodide (sp. gr. 1.7) and heated for half an hour at 100–110°, gave off methyl iodide in the exact amount required by theory. The product consisted of a mixture of acids, m. p. 175–178°.

(b) and (c) In this case the reactions were carried out with hydrogen iodide in the manner described except that the period of heating was extended to one and one-half to two hours. The product after removing the excess of hydrogen iodide was partly crystalline and partly oil and the melting point of the crystalline fraction varied considerably. As a result of attempts to resolve the crystalline fraction into its components by a prolonged process of fractional recrystallizations, acids melting at 161–163 and 183–186" were obtained but these melting points could not be improved by further recrystallizations. Although obviously representing mixtures, analyses of these lower-melting and higher-melting fractions were made and both were found to correspond in composition to the polypeptide acid expected by theory.

In general, it was found convenient not to attempt to separate this mixture of acids into its components, but after removal of the excess of hydrogen iodide to proceed with it in either of two ways: (I) to esterify by treating an alcohol solution with dry hydrogen chloride, when the ester XX was obtained as the sole crystalline product in yields averaging 20%; (II) to hydrolyze the entire product (crystals and oil) under the action of barium hydroxide, in which case the sole product consisted of the imino acid XXII in yields averaging about 75%.

Since the results of a fairly large number of experiments were practically identical, it seems reasonable to conclude that the product consisted in all cases of a mixture of isomeric acids corresponding to the above formula.

The acid XXI, m. p. 206–207.5°, was prepared by dissolving this product (obtained by treating 20 g. of the ester I with hydrogen iodide) in ether and then extracting with dilute sodium hydroxide. The aqueous alkaline extract was concentrated on a water-bath, cooled and acidified, when a gum was precipitated. The latter was taken up in ether, which when washed, dried and allowed to evaporate, deposited a fine white crystalline powder. This was further purified by recrystallization from aqueous acetone from which it separated in the form of long pale yellow needles which contained water of crystallization, and which melted at 144° with evolution of water vapor. When pure and anhydrous this acid melted at 206–207.5°. The total yield was about 3 *g.*

Anal. Calcd. for $C_{19}H_{18}O_5N_2$: N, 7.91. Found: N, 7.96, 8.05.

Ethyl **N-3-methyl-5-*p*-hydroxybenzylhydantoin-N-1-phenylacetate, XX,** m. p. 125–127°.—This substance would also appear to exist in isomeric modifications although here again difficulties were encountered in the separation of a second isomer. The preparation involved: (a) the esterification under the action of hydrogen chloride of alcohol solutions of the acid XXI and also of what seemed to be mixtures of isomeric crystalline modifications having the same composition, as for example the above-mentioned crystalline fractions melting at 161–163 and 183–186°, respectively. In every case the product consisted of a crystalline precipitate XX, m. p. 125–127°, while filtrates from this on concentration gave an oil which on long standing continued to yield additional quantities of this substance. (b) The repeated additions of alcohol (and its subsequent evaporation in open beakers on a steam-bath) to the crude product obtained by the action of hydrogen iodide on the unsaturated ester I. In this way the excess of hydrogen iodide present in the mixture acted as a catalyst in the esterification of the acids and was at the same time gradually eliminated in the form of ethyl iodide. Here again the product consisted of a crystalline ester, XX (in yields approximating 50% of the theoretical), and an oil which on standing continued to furnish additional quantities of this solid. The ester was purified by recrystallization from aqueous alcohol and also from chloroform–ether mixtures.

Anal. Calcd. for $C_{21}H_{22}O_5N_2$: N, 7.33. Found: N, 7.10, 7.08.

It may be noted that this ester appears to isomerize during the process of recrystallization since the filtrates obtained during this process on concentration yield crystalline precipitates having lower melting points than the original crystals. The ester, m. p. 125–127°, on hydrolysis under the prolonged action of barium hydroxide, is transformed into the imino acid, XXII.

The N-phenylacetic acid derivative of tyrosine,[20] XXII, m. p. 223–225° with decomposition, was prepared from XX and XXI by the action of barium hydroxide. It was also prepared by digesting the unsaturated ester I with hydrogen iodide in the presence of red phosphorus. The excess of hydrogen iodide was then removed by vacuum distillation and by digestion with small quantities of water and the residue without further purification was hydrolyzed with barium hydroxide.[21] After heating on a steam-bath for twenty-four hours, the reaction was stopped and the contents of the flask distilled with steam in order to remove the methylamine. The mixture was then filtered hot to remove barium carbonate and excess of barium hydroxide. The filtrate when exactly neutralized as to barium with sulfuric acid and separated from the precipitated barium sulfate, was evaporated to small volume at ordinary temperature. Under these conditions the imino acid separated in the form of a fine white crystalline precipitate in yields averaging 75% of the theoretical. When purified by recrystallization from alcohol it melted with decomposition at 223–225°.

Anal. Calcd. for $C_{17}H_{17}O_5N$: N, 4.44. Found: N, 4.36, 4.45, 4.46.

The acid is only very slightly soluble in hot water (1 g. in 500 cc.) and hot alcohol (1 g. in 250 cc.). It is readily changed into its copper salt from which it may be regenerated quantitatively. Other derivatives of the acid have also been prepared but these will be reported in a later paper.

The copper salt of the N-phenylacetic acid derivative of tyrosine, XXIII, m. p. 215° with decomposition, was prepared by suspending 4 g. of the acid, m. p. 223–225°, and 1.2 equivalents of basic copper carbonate in 300 cc. of water and boiling the mixture for twenty minutes or until the acid had entirely disappeared and the effervescence of carbon dioxide had ceased. The hot solution was then filtered from excess copper carbonate and on cooling yielded 4.1 g. of a blue crystalline copper salt. The filtrates from this precipitate when concentrated by heating turned dark green and then black, due to decomposition, and no further quantities of salt were obtained. After recrystallizing twice from boiling water,[22] from which it separated almost completely on cooling in the form of fine blue needles which contain water of crystallization, the substance was found to melt partially at 110° with the evolution of water vapor and completely with decomposition at 215°. The loss of water is accompanied by *a* change in color from blue to green. In order to determine the water of crystallization, the salt was heated in an air-bath at 110° to constant weight, when the following results were obtained:

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[20] Acknowledgment is made to Dorothea Naas and Anne L. White for assistance in preparing this substance.

[21] The same general procedure was followed that has been already described in connection with other similar operations. (a) Hahn and Gilman, This Journal, 47, 2951 (1925); (b) Hahn and Evans, *ibid.*, 50, 817 (1928).

[22] One gram is soluble in 100 cc. of boiling and 400 cc. of cold water.

Anal. Calcd. for $3C_{17}H_{15}O_5NCu\cdot10H_2O$: H_2O, 13.74. Found: H_2O, 13.89, 13.74, 13.37.

The green anhydrous form melts fairly sharply with decomposition at 215° and is extremely hygroscopic.

Anal. Calcd. for $C_{17}H_{15}O_5NCu$: N, 3.72. Found: N, 3.72, 3.64. Calcd. for $C_{17}H_{15}O_5NCu$: Cu, 16.89. Found:[23] Cu, 16.43, 16.53.

When the salt was dissolved in water and treated with hydrogen sulfide, it was transformed almost quantitatively into the corresponding imino acid, XXII. For example, when hydrogen sulfide was passed into a hot aqueous solution containing 2 g. of the salt, the blue color was discharged and copper sulfide was precipitated. If the solution was of sufficient volume (700 cc. for 2 g. of salt), no imino acid was precipitated at this point. The solution was filtered from sulfide, concentrated on the steam-bath to a volume of 120 cc. and cooled, when 1.5 g. of imino acid was precipitated in pure condition. Mixed melting-point determinations showed that the acid obtained in this way was identical with the original acid XXII from which the copper salt was prepared.

Summary

The introduction of the phenylacetic acid group in the N-1-position of the hydantoin ring by the synthesis of N-3-methyl-5-tyrosyl-hydantoin-1-phenylacetic acid has produced a highly labile hydantoin combination.

(a) The unsaturated derivatives exist in isomeric modifications of which two esters and three distinct acids have been isolated.' (b) The saturated derivatives also exist in isomeric modifications which may be explained on the basis of stereoisomerism. Two esters and three distinct acids were isolated, the third of which may be assumed to represent a desmotropic modification. The polypeptide-hydantoin itself also would appear to consist of a mixture of unstable forms, from which only one stable modification could be isolated. (c) The hydrolysis of the polypeptide-hydantoin resulted in the formation of a dibasic imino acid.

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[23] Copper was determined by ignition to form copper oxide. Fresenius, "Quantitative Chemical Analysis," 1904, Vol. I, p. 373.

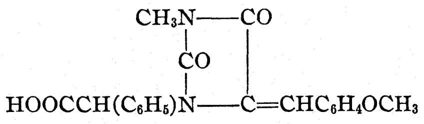
[Contribution from the Chemical Laboratory of Mount Holyoke College]

THE ISOMERISM OF CERTAIN UNSATURATED ACIDS OBTAINED IN THE SYNTHESIS OF N-3-METHYL-5-TYROSYL-HYDANTOIN-N-1-PHENYLACETIC ACID

By Dorothy A. Hahn and Elizabeth Dyer

Received February 20, 1930 Published June 6, 1930

The existence of three isomeric potassium salts and of four unsaturated isomeric acids corresponding to the formula



has been referred to in the preceding paper where the chemical relationships between these substances is indicated by means of arrows on an accompanying chart.[1] The description of their respective preparations and properties has been reserved for a separate paper largely because it seemed desirable to check the chemical properties against the absorption curves[2] of the respective substances.

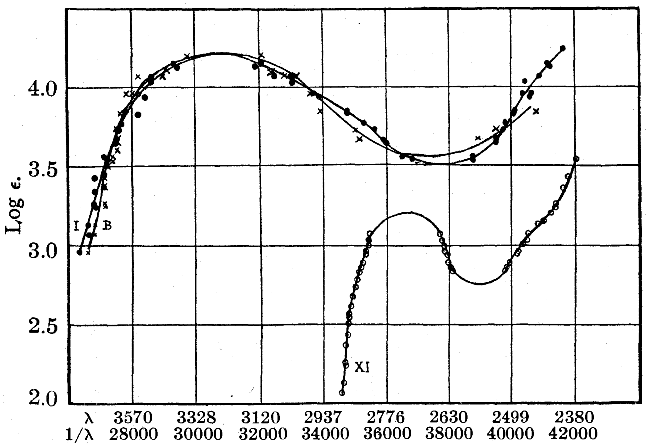


Fig. 1.—I -●-●-●- Ethyl 3-methyl-5-*p*-anisalhydantoin-1-phenylacetate, m. p. 119–120.5°. XI -○ ○-○- Ethyl 3-methyl-5-*p*-anisylhydantoin-1-phenylacetate, m. p. 112–113°. B -×-×-×- 1-Methyl-5-benzalhydantoin-3-acetic acid, m. p. 198.5–199.5°.

In the first place it may be noted that Fig. 1 offers satisfactory evidence of the similarity in constitution of ethyl-3-methyl-5-anisalhydantoin-N-

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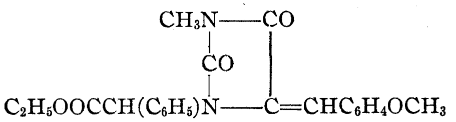
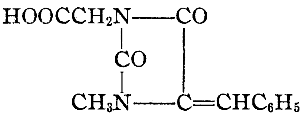
[1] Hahn and Dyer, This Journal, 52, 2494 (1930).

[2] Grateful acknowledgment is made to Dr. Emma P. Carr for advice and assistance in the spectrographic work.

1-phenylacetate, m. p. 119–120.5°, and N-1-methyl-5-benzalhydantoin-3-acetic acid, m. p. 198.5–199.5°[3]



and



This particular acid was chosen because the absorption curve actually coincides closely with that of the ester. In general the absorption curves of acids and their corresponding esters have been found to be almost identical.[4] On the other hand, the substitution of different groups in the N-1-N-3-positions of disubstituted compounds has the effect of shifting the position of the head of the band without, however, materially changing the character of the curve.[5] And if, as it seems probable, the character of the absorption of N-1-N-3 disubstituted hydantoins is practically *independent of the nature of the substituting group*,[6] this fact is of importance in establishing the configuration of the hydantoin ring in the case of all benzal and anisal unsaturated derivatives.

The curve of the saturated ester XI, also given in Fig. 1, shows a great displacement in the position of maximum absorption toward the ultraviolet and an accompanying decrease in the persistence and width of the band produced by the reduction of the double bond.

Figure 2 shows the absorption curves of two isomeric unsaturated esters (corresponding to I and II in the preceding chart) which possess bands having approximately the same width and intensity but differing slightly in position. Table I shows the wave lengths at which the intensity of absorption is a maximum and a minimum.

TABLE I

WAVE LENGTH DATA

	Log $\epsilon_{max.}$	$1/\lambda$	λ, A.	Log $\epsilon_{min.}$	$1/\lambda$	λ, A.
Ester I	4.22	30700	3257	3.50	37800	2646
Ester II	4.26	29100	3436	3.48	35650	2805

The curve of the higher-melting ester I is displaced toward the ultraviolet as compared with that of the lower-melting ester II, and this is in agreement with the relatively greater chemical stability of the former. Thus II is prepared from I only after prolonged heating of an alcohol

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[3] Hahn and Evans, THIS JOURNAL, 50, 810 (1928).

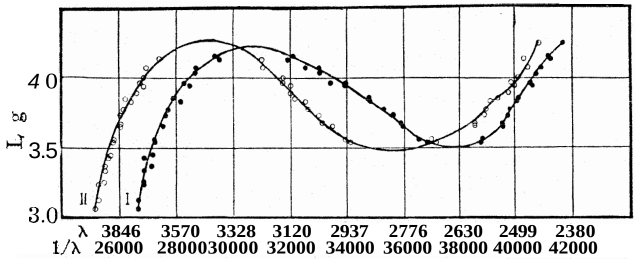
[4] Compare Figs. 2 and 3.

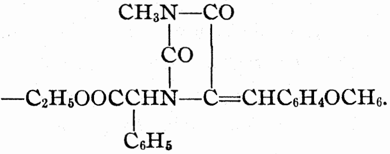
[5] Other evidence in support of this statement is to be found in unpublished spectrographic investigations of a number of different disubstituted benzal- and anisalhydantoins carried out in this Laboratory under the direction of Dr. E. P. Carr.

[6] This is interesting in view of the fact that N-3 mono-substituted hydantoins have equally characteristic and distinctly different absorption curves from N-1-N-3 disubstituted hydantoins. Compare Carr and Dobbrow, THIS JOURNAL, 47, 2963 (1925).

solution in the presence of hydrogen chloride, and reverts to **I** when allowed to stand in ether solution in the sunlight. A comparison of the above absorption curves with those of the isomeric modifications of N-1-methyl-5-benzalhydantoin-N-3-acetic acid[7] reveals a very close analogy between the two pairs of isomers and is in accord with the theory that both pairs represent geometrical modifications of the same substance.

Ethyl 3-Methyl-5-*p*-anisalhydantoin-1-phenylacetates.

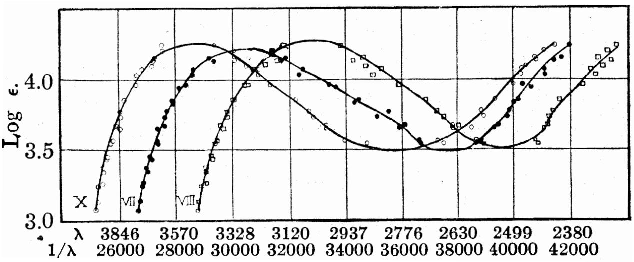


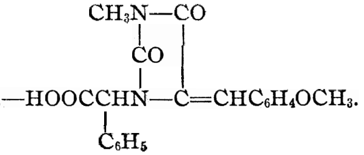


$$\begin{array}{l} \qquad\qquad\qquad\ \ CH_3N—CO \\ \qquad\qquad\qquad\quad\ \ |\qquad | \\ \qquad\qquad\qquad\quad\ CO\ \ \ | \\ \qquad\qquad\qquad\quad\ \ |\qquad | \\ C_2H_5OOCCHN—C{=}CHC_6H_4OCH_6 \\ \qquad\qquad\ \ | \\ \qquad\qquad C_6H_5 \end{array}$$

Fig. 2.—$C_2H_5OOCCHN—C{=}CHC_6H_4OCH_6$. I, m. p. 119–120.5°. II, m. p. 100.5–102°.

3-Methyl-5-p-anisalhydantoin-1-phenylacec Acids.





$$\begin{array}{l} \qquad\qquad\ \ CH_3N—CO \\ \qquad\qquad\quad\ |\qquad | \\ \qquad\qquad\ \ CO\ \ \ | \\ \qquad\qquad\quad\ |\qquad | \\ HOOCCHN—C{=}CHC_6H_4OCH_3 \\ \qquad\ \ | \\ \qquad C_6H_5 \end{array}$$

Fig. 3.—$HOOCCHN—C{=}CHC_6H_4OCH_3$. **VII, m. p. 203–204".** **VIII, m. p.** 227–229°. X, **m. p.** 178.5–180.5°

The curves for the three isomeric acids (Pig. **3)** corresponding to X, **VII** and **VIII** in the preceding chart also show bands having similar width and intensity but differing in position. The wave lengths for maximum and minimum absorption are given in Table II.

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[7] Hahn and Evans, This Journal, 50,810 (1928).

TABLE II

WAVE LENGTH DATA

	Log $\epsilon_{max.}$	$1/\lambda$	λ, Å.	Log $\epsilon_{min.}$	$1/\lambda$	λ, Å
X	4.26	28800	3472	3.49	35700	2800
VII	4.22	30550	3274	3.49	37700	2653
VIII	4.27	32900	3039	3.51	39650	2523

Similarity in the shape of the curves would indicate that these acids are closely related isomeric forms. It is, moreover, to be noted that the progressive displacement of the absorption band toward the ultraviolet from X to VII to VIII corresponds to a progressive rise in melting points accompanied by an increase in the chemical stability of the substances. The relations here are similar to those presented by the isomeric esters. For example, the acid, m. p. 178.5–180.5°, is transformed into the acid of m. p. 203–204' by the action of hydrogen chloride and the latter by a similar process into the acid of m. p. 227–229'. Reversion of the higher- to the lower-melting modifications has, however, not been observed.

In comparing the absorption curves of the esters with those of the acids it is interesting to find that the curve of II (Fig. 2) corresponds closely to the curve of X (Fig. 3) in the positions of the maximum and minimum intensities of absorption and that similarly the curve of I (Fig. 2) corresponds to the curve of VII (Fig. 3). These relationships are confirmed by the chemical data since the ester II hydrolyzes to give the acid X which in turn is readily esterified to the former, and similar transformations take place in the case of the ester I and the acid VII.

The fact that there are three acids instead of the two geometrical isomers which would normally be expected may possibly be interpreted as bringing the chemistry of the unsaturated hydantoins into line with the chemistry of the cis and trans geometrical modifications of cinnamic acid.

Experimental

N-3-methyl-5-anisalhydantoin-I-phenylaceticAcids

A. Acids Derived from the Ester I by Acid or Alkaline Hydrolysis.—VII, m. p. 203–204°, and VIII, m. p. 227–229°.—The ester melting at 119–120.5' gives on both acid and alkaline hydrolysis an acid melting at 203–204°. In both cases the yield is low, averaging 33 and 40%, respectively, of the theoretical. This may be accounted for by the tendency of all of these substances to isomerize. However, in spite of the side reactions which undoubtedly take place, clear relationships have been established between the ester I, the corresponding acid VII, and the salt III, as shown in the chart (p2496).

(1) Acid Hydrolysis.—Seven grams of the ester, m. p. 119–120.5°, was suspended in 30 cc. of boiling concd. hydrochloric acid and just enough boiling glacial acetic acid added to dissolve the oil. After heating for one hour the mixture was cooled and diluted with water, when 1.7 g. of a yellow powdery precipitate, m. p. 198–203°, separated. When the filtrates from this product were evaporated to dryness under a stream of air and the resulting gum was treated with ether, an additional 0.6 g. of the same acid

was obtained. The product was purified by recrystallization from alcohol, from which it separates as clusters of long yellow needles, m. p. 203–204".

Anal. Calcd. for $C_{20}H_{18}O_5N_2$: N, 7.65. Found: N, 7.54, 7.46.

The acid is also formed as one of the products of acid hydrolysis of the ester II. The acid is fairly soluble in hot acetone (1 g. in 35 cc.), and in hot alcohol (1 g. in 20 cc), and is less soluble in cold alcohol (1 g. in 80 cc.). It is transformed into the ester I in 90% yield when its alcohol solution is saturated with hydrogen chloride. The acid passes quickly and quantitatively into the corresponding potassium salt III when its hot alcoholic solution is treated with one equivalent of potassium hydroxide.

(2) **Alkaline** Hydrolysis.—While the above acid, VII, m. p. 203–204°, may be obtained as the principal product resulting from the alkaline hydrolysis of the ester I, two side reactions have been observed which indicate that the transformations are somewhat complicated. These are (a) the formation of a second isomeric acid, VIII, m. p. 227–229°, and (b) decomposition of the salt accompanied by the formation of methylanisalhydantoin and anisaldehyde. The latter (by varying the conditions) may be controlled and even eliminated.

The most convenient method for preparing the acid VII was to acidity an aqueous solution of the corresponding potassium salt III. Ten grams of ester I, m. p. 118–120°, was dissolved in 70 cc. of boiling 95% alcohol to which was added 1 equivalent of potassium hydroxide dissolved in 30 cc. of boiling alcohol. The solution changed color immediately from a pale yellow to a deep red; this was followed in about three minutes by a complete disappearance of color and the precipitation of a white solid. After boiling for fifteen minutes the mixture was iced and filtered. The product consisted of 4.1 g. of a salt III, m. p. 208–210° with decomposition.

Anal. Calcd. for $C_{20}H_{17}O_5N_2K$: N, 6.93. Found: N, 6.67, 6.60.

The salt, when dissolved in warm water and acidified with hydrochloric acid, passed quantitatively into the acid VII. The salt was transformed into the ester I by dissolving it in absolute alcohol and saturating the solution with hydrogen chloride, or by heating an alcohol solution with ethyl iodide. In neither case, however, was the yield more than 10% of the theoretical, due to the presence of an oily residue which would not crystallize.

Although the main product which was obtained on alkaline hydrolysis of the ester I consisted of the salt III, which was transformed into the acid VII, a second isomeric acid VIII was obtained by acidifying the alkaline filtrates (representing the combined mother liquor and washings from the salt precipitate). Under these conditions 4 g. of a white crystalline precipitate separated, m. p. 215–229°. By extracting this mixture with hot alcohol or acetone traces of the above-mentioned acid VII were removed, and the residue was found to consist of a new acid VIII, melting at 227–229". The latter was purified by recrystallization from boiling acetic acid and analyzed.

Anal. Calcd. for $C_{20}H_{18}O_5N_2$: N, 7.65. Found: N, 7.63. 7.57.

The same acid was found in small quantities among the products of alkaline hydrolysis of the ester II. It was also obtained by isomerizing the acid VII in acetic acid solution under the action of dry hydrogen chloride. This acid is soluble in boiling acetic acid (1 g. in 15 cc.) from which it separates almost completely on cooling in the form of small hard white plates. It is slightly soluble in boiling alcohol (1 g. in 100 cc.) from which it separates almost completely in the form of regular cubes. Negative results were obtained in all attempts at esterification whether by suspending the salt or acid, respectively, in alcohol and saturating the mixture with hydrogen chloride, or by heating the salt with ethyl iodide, or by application of the Schotten–Baumann reaction.

The acid VIII was transformed quantitatively into the salt IV by boiling the acid suspended in alcohol with alcoholic potassium hydroxide, After heating for twenty minutes the acid dissolved, and the solution when cooled deposited the salt in the form of clusters of colorless prisms which melted at 212° with decomposition. The salt was purified by one recrystallization from alcohol and analyzed.

Anal. Calcd. for $C_{20}H_{17}O_5N_2K$: N, 6.93. Pound: N, 6.72, 6.68.

The salt was completely soluble in water and its aqueous solution when acidified passed quantitatively into the acid VIII.

The statement has been made that under certain conditions alkaline hydrolysis of the ester I is accompanied by decomposition with the formation of methylanisalhydantoin and anisaldehyde. For example, in a few experiments where the hydrolysis was carried out in 25 or 50% aqueous alcoholic mixtures, it was observed that after the salt III had separated as described above, the alkaline filtrate behaved in a curious way. Thus, when concentrated to one-third its volume to remove the alcohol, and then diluted with water to the original volume, precipitation of a neutral product, m. p. 212–215°, took place. This was fully identified as methylanisalhydantoin. The filtrate from this precipitate when acidified yielded the usual quantity of the acid VIII. Decomposition could be eliminated by carrying out the hydrolysis in 95% alcohol and acidifying immediately without concentrating to remove the alcohol. The same decomposition was brought about when the pure salt III was heated for six days in a 95% alcohol solution containing 0.1 equivalent of alkali or for three hours in a weakly alkaline aqueous solution. In both cases about 10% of the salt was decomposed into methylanisalhydantoin and at the same time a secondary decomposition with the splitting off of anisaldchyde took place. The anisaldehyde was separated from the alkaline mixture by steam distillation, and its identity was established by its odor, its reaction with Tollens' reagent, and its conversion into anisic acid, which was compared with a pure laboratory specimen.

B. Acids Derived from the Ester II by Acid or Alkaline Hydrolysis.—VII, m. p. 203–204°; IX, m. p. 58–62°; and X, m. p. 178.5–180.5'.

(1) Acid Hydrolysis.—The products obtained by acid hydrolysis of the ester II consisted of a new acid, X, along with small quantities of the acid VII. For example, 2 g. of the ester II, m. p. 100.5–101.5°, was suspended in 25 cc. of hydrochloric acid and about 20 cc. of acetic acid was added gradually accompanied by boiling and shaking. After the material had dissolved completely, the solution was boiled for one hour and then cooled. The product (which separated as an oil) was precipitated completely by the addition of water, the acid solution decanted, the oil washed with water and finally taken up with alcohol. This solution on dilution with water yielded 1.7 g. of a somewhat granular precipitate, m. p. 75–145°. The acids composing this mixture were separated by extraction with small quantities of ether. The insoluble residue consisted of an acid, m. p. 199–202°, which when pure was identified as the acid VII. The ether extract on evaporation deposited a hard yellow gum which after recrystallization from alcohol yielded a crystalline acid, m. p. 178.5–180.5° (X).

Anal. Calcd. for $C_{20}H_{18}N_2O_5$: N, 7.65. Found: N, 7.54, 7.71.

This acid is soluble in boiling alcohol (1 g. in 15 cc.) and less soluble in cold alcohol (1 g. in 50 cc.), from which it crystallizes in the form of hard bright yellow plates. Its aqueous solution neutralizes the theoretical quantity of standard base. When dissolved in alcohol previously saturated with hydrogen chloride and boiled for one hour, it is transformed into the ester II (yield 84% of the theoretical). Esterification is accompanied also by isomerization, since a small quantity of the ester I is also always formed. The acid X is partially changed into the isomeric acid VII on prolonged boiling of its acetic acid solution with concentrated hydrochloric acid.

(2) Alkaline Hydrolysis.—The potassium and sodium salts V and VI were prepared, respectively, by boiling an alcohol solution of the ester II with 1.2 equivalents of alco-

holic potassium hydroxide or with a corresponding amount of sodium alcoholate. In each case the reaction was accompanied by a color change first to dark red and then to light yellow and was complete after boiling from fifteen to twenty minutes. Quantitative amounts of salt were precipitated from their respective solutions upon cooling, and after recrystallization from water the potassium salt melted at 192–194° with decomposition and the sodium salt at 128–132° with decomposition.

Anal. Calcd. for $C_{20}H_{17}O_5N_2K{\cdot}2H_2O$: N, 6.36. Found: N, 6.26, 6 22. Calcd. for $C_{20}H_{17}O_5N_2Na{\cdot}H_2O$: N, 6.90. Found: N, 6.83, 6.73.

When an aqueous solution of either of the above salts was acidified with hydrochloric acid, a yellow granular precipitate was formed. This, when washed with water and dried in the air, yielded a pale yellow powder which melted at 58–62°. On further heating it solidified completely at 130° and then remelted to a clear liquid at 178–180°. A sample when heated in an oven at 50° did not change in weight but was then observed to melt at 88–178°. Since it was impossible to purify the substance by recrystallization, analyses were made using freshly precipitated samples both before and after heating at 50°.

Anal. Calcd. for $C_{20}H_{18}O_5N_2$: N, 7.65. Found: N, 7.54, 7.46, 7.42.

Since these results agree very closely with those calculated, it may be assumed that the substance represents an unstable isomeric modification of the acid X into which it gradually tends to rearrange. This is confirmed by the fact that an acid, m. p. 178.5–180 5°, which was fully identified as X is formed (a) when the acid, m. p. 58-62", is heated, (b) when it is allowed to stand at room temperature for several days and *(c)* when it is dissolved in cold solvents such as alcohol, chloroform, ether or acetic acid. In every case the substance dissolved readily to give a clear solution which in a few minutes became cloudy and then yielded a fine crystalline powder which was found to consist of the acid X in pure condition. A spectrographic analysis, conducted as rapidly as possible with a specimen of the substance melting at 58–62°, gave an absorption curve which was identical in all respects with that of the acid X, m. p. 178.5–180.5°.

Spectrographic measurements were made with a Hilger quartz spectrograph (E 36) according to the quantitative method of Henri.[8] The substances to be examined, having been purified by repeated crystallization from absolute alcohol, were dissolved in specially purified absolute alcohol.[9] Solutions of 0.0001 and 0.0002 M concentration were placed in Baly quartz tubes and exposed to a spark from iron electrodes for periods of forty to sixty seconds, the thickness of the solution varying from 6 to 60 mm. For purposes of comparison the same thicknesses of solvent were exposed for periods of ten seconds each. Lumière and Jougla photographic plates were used. The extinction coefficients were calculated from the expression

$$\epsilon = \frac{n}{cd} \log \frac{t_{\text{solution}}}{t_{\text{solvent}}}$$

where ϵ equals the molecular extinction coefficient, n is a constant depending on the photographic plates (*i. e.*, 0.9), *c* is molar concentration, d is thickness in centimeters and *t* is period of exposure in seconds.[10]

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[8] Henri, "Études de Photochemie," Gauthier-Villars, Paris, 1919, p. 5.

[9] Castille and Henri, Bull. *soc. chim. biol.*, 6, 299 (1924).

[10] Acknowledgment must be made to Miss Katherine M. Haring for assistance in making some of these measurements.

Summary

The fact that N-1-N-3-disubstituted unsaturated hydantoins with different groups in union with the nitrogen show practically the same absorption spectra may be applied in determining the configuration of the molecule.

A strikingly close analogy has been observed between the relationship indicated by a comparison of absorption curves and the chemical properties of the substances studied.

Three closely related isomers have been discovered where only two might normally be predicted on the basis of geometrical isomerism.

SOUTH HADLEY, MASSACHUSETTS

[A COMMUNICATION FROM THE LABORATORIES OF ORGANIC AND AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE PREPARATION AND ANTIRACHITIC ACTIVATION OF SOME DERIVATIVES OF ERGOSTEROL AND CHOLESTEROL

BY D. W. MACCORQUODALE, HARRY STEENBOCK AND HOMER ADKINS

RECEIVED FEBRUARY 21, 1930 PUBLISHED JUNE 6, 1930

Inasmuch as biochemical tests revealed that extraction of yeast and plant materials with alcohol, or even with concentrated solutions of potassium hydroxide in alcohol, failed to free them of substances capable of antirachitic activation (unpublished work) it occurred to us that ergosterol was probably present therein in the form of derivatives. Speculation concerning the possible nature of such derivatives led us to attempt the synthesis of the d-glucoside of ergosterol and N-ergosterol glycine, as representatives of carbohydrate and protein substances, respectively. We were successful in our attempt to synthesize the carbohydrate compound, but failed with the latter. In order to avoid waste of ergosterol, preliminary experiments were always carried out with cholesterol.

The glucoside of cholesterol was first described by Salway[1] who obtained it by the condensation of the sterol with tetra-acetylbromoglucose by means of dry silver oxide, and subsequent saponification of the acetyl derivative. This method was found to be entirely satisfactory for the preparation of the glucoside of ergosterol, the only precaution necessary being the rigid exclusion of moisture.

A large number of experiments were made in an unsuccessful attempt to obtain an ergosteryl halide which, it was hoped, might be condensed with the amino acids to produce secondary amines. Darzens' method[2] for the preparation of halides by treatment of the appropriate alcohol with thionyl chloride in the presence of pyridine or other tertiary base when applied to

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[1] Salway, J. *Chem. Soc.*, 103, 1026 (1913).

[2] Darzens, *Compt.* rend., 152, 1314 (1911).

cholesterol yielded a white crystalline compound which analysis showed to be cholesteryl sulfite. After this work was completed a paper appeared by Daughenbaugh and Allison[3] in which they described the preparation of cholesteryl sulfite by Darzens' method. The properties given by them for this compound are in excellent agreement with those found by us. Various proportions of ergosterol with thionyl chloride and pyridine in dry ether gave small yields of what was apparently the sulfite or in other cases the chlorosulfite. In dry chloroform the reaction product was an oily tar. Phosphorus trichloride and phosphorus tribromide in dry benzene and dry 1,4-dioxane produced small yields of organic compounds containing phosphorus. Phosphorus tri-iodide in carbon disulfide also produced an organic phosphorus compound. None of these was further investigated.

Efforts were next directed toward the preparation of an ergosteryl ester of an amino acid. Abderhalden and Kautsch[4] prepared the cholesteryl ester of glycine by reacting cholesterol with glycyl chloride hydrochloride in dry chloroform and liberating the ester from its salt by means of alkali. Attempts to carry out this reaction with ergosterol proved unsuccessful due to the destructive action of the hydrogen chloride liberated in the reaction. The use of pyridine to avoid this proved ineffective because it reacted with the glycyl chloride hydrochloride liberating glycyl chloride which immediately underwent condensation. When the amino group was protected by benzoylation, good yields of cholesteryl and ergosteryl hippurates were obtained.

Schmidt, Knilling and Ascherl[5] have used acetobromo-amide as a reagent for the addition of hypobromous acid to the ethylene bond and it seemed that this method might serve to throw additional light on the nature of the unsaturation in ergosterol. The reaction was found to work very smoothly in the case of cholesterol, practically quantitative yields of the bromohydrin being produced, but with ergosterol decomposition was rapid and extensive.

Heilbron and Sexton[6] have described the results of some experiments on the catalytic hydrogenation of the free ergosterol with a palladium catalyst. When this paper appeared we were engaged in some similar experiments using the platinum catalyst of Voorhees and Adams and we likewise found that at a pressure just slightly greater than atmospheric two moles of hydrogen were absorbed with the formation of the a-ergostenol of Reindel and Walter.[7] The reductions were carried out in a semi-micro hydrogenation apparatus at room temperature, and the solvents used were ethyl acetate, ethyl alcohol and glacial acetic acid, all three solvents giving the same re-

[3] Daughenbaugh and Allison, THIS JOURNAL, 51, 3666 (1929).

[4] Abderhalden and Kautsch, *Z. physiol. Chem.*, **65**, 69–77 (1910).

[5] Schmidt, Knilling and Ascherl, *Ber.*, **59B**, 1279–1282 (1926).

[6] Heilbron and Sexton, *J. Chem. Soc.*, 921–926 (1929).

[7] Reindel and Walter, *Ann.*, 460, 212 (1928).

sults. In a typical experiment, 0.1093 g. of ergosterol dissolved in 40 cc. of glacial acetic acid was shaken with hydrogen and 0.100 g. of catalyst previously reduced and saturated with hydrogen. At the end of twenty-five minutes the contraction amounted to 16.9 cc. (calcd. for two moles, 17.5 cc.) and after an additional forty-five minutes it was 17.2 cc. There was no break in the curve to indicate the formation of the dihydroergosterol

Experimental

Tetra-acetylbromoglucose.—This was prepared by the method of J. K. Dale.[8] It was found that a mixture of dry ether and dry petroleum ether was a much better solvent for recrystallization than ether alone. From the mixed solvent the product was obtained in beautiful white needle-like crystals which melted at 88–89°.

Ergosterol-*d*-glucoside.—Ergosterol, obtained from The Fleischmann Company was purified by recrystallization from a mixture of alcohol and benzene as described by Bills and Honeywell.[9] Two crystallizations gave a product which had $[\alpha]_D^{20}$ $-131.5°$ and melted at 164°. This ergosterol was dried at room temperature and 2-mm. pressure for one hour and then at 80° and the same pressure for fifteen minutes. Then 2.00 g. of this was dissolved in 100 cc. of thoroughly dried ether and 3.00 g. of pure freshly recrystallized tetra-acetylbromoglucose and 3.00 g. of dry Freshly precipitated silver oxide added. This was shaken for about eight hours, after which the container was centrifuged to collect the silver bromide and silver oxide at the bottom. The clear ethereal solution was poured through a filter and the ether distilled off on the water-bath. The crude tetra-acetyl-ergosterol-d-glucoside thus obtained was crystallized once from 95% alcohol. The partially purified product was dissolved in boiling 95% alcohol and an excess of hot 10% alcoholic potash was added. The glucoside precipitated immediately and after warming for a few minutes on the water-bath the product was filtered from the hot solution and washed thoroughly with boiling 95% alcohol. For complete purification it was boiled with redistilled pyridine and filtered from a small amount of insoluble material. The filtrate was diluted somewhat with distilled water and allowed to cool, whereupon the glucoside separated in pure white crystals which were filtered off and washed with cold dilute pyridine and then with 95% alcohol. The yield was 0.94 g. Another recrystallization from dilute pyridine yielded 0.84 g. of product. The glucoside is insoluble in water, alcohol, ether, chloroform, acetone, benzene and ethyl acetate. It dissolves with difficulty in hot amyl alcohol and glacial acetic acid, and with ease in hot pyridine. It melts at 308" (corr.) with decomposition; $[\alpha]_D^{25}$ -98.5 when $C = 1$ in pyridine.

Anal. Calcd. for $C_{33}H_{52}O_6$: C, 72.75; H, 9.63. Found: C, 72.64; H, 10.07.

Upon hydrolysis with hydrochloric acid in a mixture of amyl alcohol and ethyl alcohol, glucose and isoergosterol are formed.

Tetra-acetyl-ergosterol-d-glucoside.—One gram of pure ergosterol-d-glucoside was boiled for thirty minutes with 10 cc. of pure acetic anhydride, the excess of the latter then being removed by distillation under diminished pressure on the water-bath. The residue was dissolved in 25 cc. of hot absolute alcohol and filtered through a hot funnel. Upon cooling, the filtrate deposited the tetra-acetyl-ergosterol-d-glucoside in fine white needle-like crystals. This product was filtered off, washed with ice-cold absolute alcohol and the crystallization repeated. The yield was 0.80 g. of product which melted at 167° corrected. It dissolves readily in ether, acetone, ethyl acetate, chloroform,

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[8] Dale, THIS JOURNAL, 38, 2187 (1916).

[9] Bills and Honeywell, *J. Biol. Chem.*, 80, 12 (1928).

benzene and glacial acetic acid. It is fairly soluble in hot alcohol but crystallizes out almost completely on cooling; $[\alpha]_D^{25}$ −43.0° when C = 1 in chloroform.

Anal. Calcd. for $C_{41}H_{60}O_{10}$: C, 69 06; H, 8.49. Found: C, 69.43; H, 8.60.

Cholesteryl Hippurate.—One gram of dry cholesterol was dissolved in 5 cc. of dry chloroform and heated on the water-bath for half an hour with 0.60 g. of hippuryl chloride. The solution was then evaporated to about 3 cc. and a large excess of hot methyl alcohol added. On cooling the cholesteryl hippurate separated in small spherical clusters of needles. The yield was 1.35 g. It was recrystallized three times from methyl alcohol containing a little chloroform and then melted at 153–154° corrected; $[\alpha]_D^{25}$ −30.5" when C = 1 in chloroform. It dissolves in about twenty-five parts of methyl alcohol and separates on cooling in small roset-like clusters of needles. From 80% ethyl alcohol it separates in long hair-like needles. It dissolves easily in chloroform, acetone, benzene, ethyl acetate and glacial acetic acid. It is insoluble in water. On saponification with dilute alcoholic potassium hydroxide it yields cholesterol and hippuric acid.

Anal. Calcd. for $C_{36}H_{53}O_3N$: N, 2.56. Found: N, 2.60.

Ergosteryl **Hippurate.**—One-half gram of pure ergosterol ($[\alpha]_D^{25}$ −131.5°) and 0.30 g. of hippuryl chloride were dissolved in 3 cc. of dry chloroform containing 0.5 cc. of pure dry pyridine and heated on the water-bath for half an hour. Then 25 cc. of dry methyl alcohol was added and the brown solution chilled in ice and salt. The crystalline ergosteryl hippurate was filtered off and washed with methyl alcohol. The yield of crude dry product was 0.63 g. It was recrystallized once from 95% ethyl alcohol containing a little chloroform and then three times from pure acetone. This gave 0.24 g. of product which was dried at 80° and 2 mm. and then melted at 166–167° corrected. Its solubility in ethyl alcohol roughly corresponds to that of cholesteryl hippurate in methyl alcohol and it crystallizes in the same manner. It dissolves readily in benzene and chloroform. It is moderately soluble in acetone, ethyl acetate and hot ethyl alcohol. It is only sparingly soluble in cold ethyl alcohol and almost insoluble in methyl alcohol. It does not dissolve in water. $[\alpha]_D^{25}$ −67.5°, when C = 1 in chloroform. On saponification with alcoholic potassium hydroxide it yields ergosterol and hippuric acid.

Anal. Calcd. for $C_{36}H_{49}O_3N$: N, 2.58. Found: N, 2.30.

Cholesterol **Bromohydrin.**—Three grams of cholesterol was dissolved in 8 cc. of pure chloroform and 8 cc. of distilled water was added. Then 1.10 g. of acetobromoamide was added and the mixture shaken at room temperature until the water layer no longer affected starch–iodide paper. This required about six hours. The chloroform layer was washed twice with distilled water and dried over anhydrous sodium sulfate. after which it was filtered into a 100-cc. distilling flask and the solvent removed by distillation in a vacuum at room temperature. The flask was finally heated for one and one-half hours on the water-bath to remove the last traces of chloroform. The product swelled up to a light fluffy solid mass which was easily broken up and removed from the flask. The yield of almost pure white product was 3.12 g. It melted, but not sharply, at about 85° and underwent rapid decomposition at a slightly higher temperature. It is very soluble in benzene, chloroform, ethyl acetate, ethyl alcohol, methyl alcohol, petroleum ether, ethyl ether, acetone and glacial acetic acid. It is insoluble in water. No suitable solvent was found for recrystallization.

Anal. Calcd. for $C_{27}H_{47}O_2Br$: Br, 16.53. Found: Br, 16.62.

Biological Tests

The biological tests were carried out with rats. They were young animals raised under standard conditions to a weight of about 60 g. in our stock colony. After having attained this weight they were transferred to a rickets-producing diet for three to four weeks, by which time they had always developed a very pronounced degree of rickets. They were then taken for test. The diet used was our Ration 2965[10] consisting of yellow corn 76, wheat gluten 20, calcium carbonate 3 and sodium chloride 1.

When the animals were taken for the curative tests the afore-mentioned ration had incorporated in it the sterol preparation mixed in the desired quantity with 50 g. of the ration. This was fed ad *libitum*, daily consumption records being taken. When the 50 g. was completely consumed the unsupplemented ration was fed until ten days had elapsed from the beginning of the experimental period. The animals were then killed and the distal ends of the radii and ulnae examined for the deposition of calcium phosphate in the rachitic lesions.[10]

TABLE I

CALCIFICATION WITH IRRADIATED STEROL PREPARATIONS

Rat	Mg.	Dietary addition	Initial wt., g.	Final wt., g.	Av. consumption, g.	Line test
9509	0.01	Cholesterol glucoside Mc 185	87	92	10.0	−
9510	.10	Cholesterol glucoside Mc 185	73	78	7.5	−
9511	2.00	Cholesterol glucoside Mc 185	77	82	9.5	−
9515	0.01	Ergosterol glucoside Mc 193	88	95	10.0	−
9516	.10	Ergosterol glucoside Mc 193	100	104	9.2	++
9517	2.00	Ergosterol glucoside Mc 193	84	80	9.2	++
9520	2.00	Acetyl ergosterol glucoside Mc 194	85	82	7.5	+++
9523	2.00	Acetyl ergosterol glucoside Mc 195	88	89	8.1	+++
9784	0.01	Ergosterol d-glucoside Mc 200	80	73	6.9	++
9785	0.10	Ergosterol d-glucoside Mc 200	72	75	6.9	++ or +++
9786	2.00	Ergosterol d-glucoside Mc 200	84	86	6.4	++++
9792	0.01	Isoergosteryl acetate Mc 203	91	107	9.3	−
9794	2.00	Isoergosteryl acetate Mc 203	74	77	8.7	−
9839	0.10	Isoergosterol Mc 204	87	97	6.3	−
9842	2.00	Isoergosterol Mc 204	90	98	6.9	−
9969	0.01	α-ergostenyl acetate Mc 209	79	80	5.1	++++
9970	.10	a-ergostenyl acetate Mc 209	84	90	6.1	++++
9972	.01	α-ergostenol Mc 210	82	78	5.7	++++
9973	.10	a-ergostenol Mc 210	84	70	4.0	++++
217	.10	Ergosteryl hippurate Mc 221	94	90	7.4	+++
220	.10	Cholesteryl hippurate Mc 219	80	87	7.0	−
9975	.01	Ergosterol d-glucoside Mc 212	85	90	9.0	+++
9976	.10	Ergosterol d-glucoside Mc 212	85	95	7.5	++++
9977	2.00	Ergosterol d-glucoside Mc 212	87	98	5.7	++++

Key to table: − = wide rachitic metaphyses; + = narrow line; ++ = medium metaphyses or medium line; +++ = wide line or narrow metaphyses; ++++ = almost complete healing.

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[10] Steenbock and Black, *J. Biol. Chem.*, 64, 263 (1925).

For their activation the sterol derivatives were exposed to the radiation of a Hanovia Alpine Sun Lamp at a distance of 25 cm. from the burner. In order to secure thorough exposure and to facilitate subsequent mixing with the ration, 10 mg. of the preparation was ground in a mortar with 990 mg. of sucrose. The mixture was then spread out on a glass dish measuring 22.2 by 16.5 cm. and irradiated with mixing at intervals of fifteen minutes for a period of one hour. The mixing of the preparations with sucrose is permissible because sucrose is not antirachitically activatable. The results of the tests are listed in Table I. Because the various preparations differ as to purification, treatment, etc., a brief description of each is necessary.

Cholesterol-d-glucoside, Mc 185.—This was prepared by Salway's method,' the cholesterol used having a melting point of 147–148°. The glucoside was crystallized four times from dilute pyridine and melted at 265–270° with decomposition.

Ergosterol-*d*-glucoside, Mc 193.—This preparation was made from an incompletely purified specimen of ergosterol having a melting point of 157–159° (short thermometer). The crude glucoside was recrystallized once from pure dilute pyridine and was then extracted for one hour with pure dry ether in a Soxhlet extractor. The crystallization and extraction were repeated after which the dry product had a melting point of 308" (corrected) with decomposition.

Tetra-acetyl-ergosterol-d-glucoside, Mc 194.—A portion of the glucoside Mc 193 was not extracted the second time with ether but was acetylated by boiling with acetic anhydride. The product was recrystallized twice from absolute alcohol and melted at 163° (uncorr.).

Tetra-acetyl-ergosterol-d-glucoside Mc 195.—The preparation of this was identical with that of Mc 194 except that the ergosterol used was of a fairly high degree of purity having a specific rotation of −128° and a melting point of 161 5–162.5° (short thermometer).

Ergosterol-d-glucoside **Mc** 200.—The ergosterol used for this preparation was rather crude, having a melting point of 152–156" (short thermometer). Purification of the glucoside was the same as that of Mc 193.

Isoergosteryl Acetate **Mc** 203.—This was prepared by treatment of a chloroform solution of ergosteryl acetate with dry hydrogen chloride according to the directions of Reindel, Walter and Rausch.[11] The product was recrystallized three times from a mixture of methyl alcohol and ethyl acetate (4:1) and then twice from glacial acetic acid. The crystals began to sinter at 128° and melted at 131–132° (short thermometer).

Isoergosterol **Mc** 204.—A sample of ergosteryl acetate which had a melting point of 174° uncorrected was treated with hydrogen chloride in chloroform solution and the isoergosteryl acetate recrystallized twice from methyl alcohol and ethyl acetate (4:1) and once from glacial acetic acid. The ester was saponified with alcoholic potash and the isoergosterol recrystallized twice from a mixture of methyl alcohol and ethyl acetate (4 :) The crystals were found to have a melting point of 145–146° whereas Reindel, Walter and Rausch[11] give the melting point of their compound as 135–136°. The reason for this discrepancy became clear with the appearance of a paper by Heilbron and Spring[12] in which these authors have shown that the isoergosterol of Reindel, Walter and Rausch is a mixture of two isomers, a-isoergosterol melting at 143–144°, and β-

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[11] Reindel, Walter and Rausch, *Ann.*, 452, 34 (1927).

[12] Heilbron and Spring, J. *Chem. Soc.*, 2807 (1929).

isoergosterol melting at 135°. Clearly our compound was the a-isomer which we had separated by the repeated crystallization.

α-Ergostenyl Acetate Mc 209.—The ergosterol used was the same as that used for preparation Mc 195. It was acetylated and the acetate reduced catalytically in glacial acetic acid. The a-ergostenyl acetate was purified by recrystallization first from methyl alcohol and ethyl acetate (4:1) and then from methyl alcohol and ether (4:1). It melted at 110–111° (short thermometer).

a-Ergostenol Mc 210.—The ergosterol was the same as for Mc 209. It was hydrogenated in glacial acetic acid and then precipitated with water. The product was warmed with alcoholic potash, diluted and chilled. It was then recrystallized twice from methyl alcohol and then melted at 130–131° (short thermometer).

Ergosteryl Hippurate Mc 221 and Cholesteryl Hippurate Mc 219.—These were the preparations previously described in detail.

Ergosterol d-Glucoside Mc 212.—This was prepared from highly purified ergosterol. Its preparation has already been described in detail.

These data show that isoergosterol, isoergosteryl acetate, cholesterol-*d*-glucoside and cholesteryl hippurate are entirely unactivatable. The glucoside, the tetra-acetylglucoside and the hippurate of ergosterol are shown to be antirachitically activatable, although to a somewhat less degree than the free sterol. The tests show a-ergostenol and a-ergostenyl acetate to be activatable but we do not wish these results to be accepted as final. The feeding tests of these compounds were unsuccessful in several cases as the consumption of the ration was incomplete. However, this apparently was not due to any properties peculiar to the ergostenol, for at the same time the consumption of a ration containing ergosterol glucoside was also incomplete.

Summary

1. Five new compounds, ergosterol-d-glucoside, tetra-acetyl-ergosterol-d-glucoside, ergosteryl hippurate, cholesteryl hippurate and cholesterol bromohydrin have been prepared and their properties described.

2. Ergosterol-*d*-glucoside, tetra-acetyl-ergosterol-d-glucoside and ergosteryl hippurate and perhaps a-ergostenol have been shown to be antirachitically activatable by ultraviolet light, while cholesterol-d-glucoside, cholesteryl hippurate, isoergosterol and isoergosteryl acetate have been shown to be unactivatable.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE HYGIENIC LABORATORY, U. S. PUBLIC HEALTH SERVICE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXIX. THE PREPARATION OF CRYSTALLINE TURANOSE[1]

BY C. S. HUDSON AND EUGEN PACSU

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Alekhine[2] found that when the trisaccharide melezitose is gently hydrolyzed by weak acid solutions there results as one of the products a disaccharide to which he gave the name turanose. He observed that turanose is dextrorotatory and he states that it melts at 65–70° and is very hygroscopic; this description indicates in the light of our present results that his preparation must have been an amorphous substance. Alekhine obtained only glucose by the complete hydrolysis of melezitose with strong acids and he concluded that turanose is a di-glucose. This inference was later revised by G. Tanret,[3] who obtained both glucose and fructose from the hydrolysis of turanose. Tanret describes turanose as a white powder consisting of extremely hygroscopic round grains containing one-half molecule of alcohol of crystallization, melting at 60–65° and showing $[\alpha]_D$ +71.8, without mutarotation. His description indicates in the light of our results that the substance was not obtained in crystalline condition. Alekhine observed that turanose is a reducing sugar; decision as to whether it is a glucosido-fructose or a fructosido-glucose was made by Kuhn and Von Grundherr,[4] who found that it is not oxidized by alkaline hypoiodite solution and must consequently be a glucosido-fructose.

This partial determination of the structure of turanose leads at once to some very interesting speculations concerning the structure of melezitose. Since melezitose is a non-reducing sugar, its structure must be indicated as glucose< >fructose>glucose, where the disaccharide>fructose>glucose is turanose. What is the identity of its other potential disaccharide, which must be a non-reducing sugar, glucose< >fructose? Obviously this sugar may be sucrose. If such is not the case it must be an isomer closely related to sucrose. Kuhn and Von Grundherr have found that certain enzyme preparations which hydrolyze sucrose also split melezitose into glucose and

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[1] Publication authorized by the Surgeon General of the U. S. Public Health Service. The crystallization of turanose was reported by the authors at the April, 1929, meeting of the National Academy of Sciences and a short article was published in *Science*, 69, 278 (1929). No. XXVIII of this series was published in THIS JOURNAL, 52, 2106 (1930).

[2] Alekhine, *Ann. phys. chim.*, *18*, 532 (1889).

[3] Tanret, Bull. *soc. chim.*, **35**, 816 (1906).

[4] Kuhn and Von Grundherr, ***Ber.***, 59, 1655 (1926); Bougault, *J. pharm. chim.*, 16, 97 (1917); Votoček and Nemeček, Z. *Zuckerind. Böhmen*, **34**, 399 (1910); Nef, *Ann.*, 403, 204 (1914).

turanose and they conclude that melezitose is probably a derivative of sucrose. When these authors published their observations, one of us (C. S. H.) made the following calculations from the application of the isorotation rules to the rotations of the substances in question. It has long been known[5] that the mixture of the forms of glucose and fructose which are initially liberated through the hydrolysis of sucrose by invertase possesses the same rotation as sucrose, that the glucose form is ordinary a-glucose ($[\alpha]_D$ 113) and that consequently the fructose form is one having an $[\alpha]_D$ value of about $+17$. This form must be a β-fructose; if it were an a-fructose the mixture immediately resulting from the hydrolysis would show a much lower dextrorotation than sucrose, which is not the fact. Assume now with Kuhn and Von Grundherr that melezitose is a derivative of sucrose and apply similar considerations. The initial products of its hydrolysis must be a-glucose (113) and a β-form of turanose; this mixture must show the same rotation as melezitose ($[\alpha]_D$ 88.6). The $[\alpha]_D$ value of this hypothetical β-turanose is obtained from these data, when the molecular weights are introduced, as $((88.6)(504) - (113)(180))/342 = 71$. This calculated value is quite near the rotation of turanose which l'anret has measured (71.8). Obviously the measurement applies to stable solutions of turanose. It seemed therefore from the calculations that melezitose might indeed be a derivative of sucrose and that if such is the case turanose might be found to be a ketose which, like sorbose, tagatose and mannoketoheptose, would not exhibit mutarotation. Obviously the existence or absence of mutarotation could only be determined from the study of truly crystalline turanose, but since Tanret believed that he had the crystalline sugar in hand and found no mutarotation, the calculations appeared to be substantiated throughout. However, it was not considered wise to publish these considerations at the time because of the following uncertainty: the statement by l'anret that his turanose preparation melted at as low a temperature as 60–65° and was exceedingly hygroscopic and the fact that accurately discernible crystals were not reported suggested that the substance was really amorphous because the reported properties would be most unusual for a pure crystalline

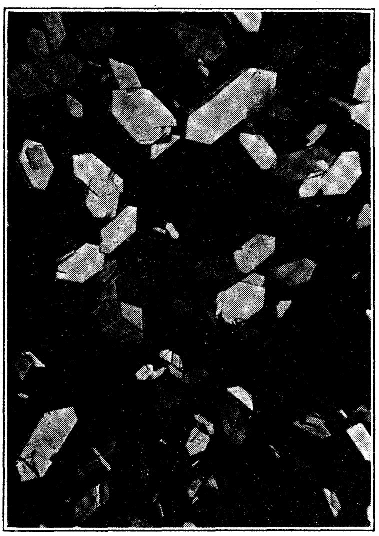

Fig. 1.—Crystals of turanose in polarized light

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[5] Hudson, THIS JOURNAL, 31, 655 (1909); see also *ibid.*, 52, 1715 (1930).

disaccharide. Indeed, Bridel and Aagaard[6] have expressed the conviction that Tanret did not crystallize turanose. It was decided, therefore to await the production of further experimental evidence. This has fortunately been obtained lately in an unexpected way, as will now be described. In 1918 one of us found an abundant supply of the rare melezitose in a certain kind of honey-dew honey[7] and from it he prepared a small quantity of sirupy turanose in the hope of crystallizing it. Other samples of turanose sirup were prepared subsequently from this stock of melezitose by other workers in the same laboratory. Recently it was observed by D. H. Brauns that one of these sirups, the exact history of which is not now known, had crystallized after standing many years. By the use of these crystals to nucleate turanose sirups which we have lately prepared from melezitose, it has been possible to obtain a rapid crystallization of the sugar in abundant quantities.[8]

The physical properties of crystalline turanose differ entirely from those reported by G. Tanret and there can no longer be any doubt that his preparation was an amorphous material. The sugar is readily purified by recrystallization from hot methyl alcohol, in which it is moderately soluble. Its melting point is 157°, it crystallizes in well-formed prisms with many faces developed (see photograph), its composition is $C_{12}H_{22}O_{11}$ and it is not hygroscopic. We were surprised to find that it exhibits a large and rapid

TABLE I

MUTAROTATION OF TURANOSE AT 22° IN AQUEOUS SOLUTION (CONCENTRATION, 3.928 G./100 Cc.)

Time, minutes	$[\alpha]^{22}_{D}$	$k = \frac{1}{t} \log \frac{R_\infty - R_0}{R_\infty - R}$
0	(+22 0)	..
4	+53 5	..
5	+58 1	0 103
6	$61 4	.098
7	$64.5	101
8	+66 2	.095
9	$68 2	.091
10	$69 7	.098
11	f70 6	.095
12	+71 7	098
13	$72 4	.097
14	+73 0	098
25	$75 3	
60	$75 3	Average .097

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[6] Bridel and Aagaard, Bull. *soc. chim. biol.*, **9**, 884 (1927).

[7] Hudson and Sherwood, THIS JOURNAL, 42, 116 (1920).

[8] During the hot dry season in early July, 1928, an unusually large flow of honey-dew honey occurred in apiaries around Washington, D. C., and we were able to prepare five kilograms of melezitose from such honey kindly supplied by the Office of Bee Culture Investigations, U. S. Department of Agriculture, from their apiary at Somerset, Maryland.

mutarotation, from the direction of which it is inferred that the sugar is a beta modification. The designation is provisional, however, because it is not excluded that a ring shift may occur during the mutarotation. The course of the change is shown in the table; it follows closely the unimolecular law and consequently the initial rotation can be obtained with fair accuracy by extrapolation. The value of the final rotation (75.3) shows that the previous estimates by Tanret (71.8) and by Bridel and Aagaard (72–73) from the study of amorphous materials were fair approximations.

Let us return now to the theoretical considerations. Observation shows that the form in which turanose has crystallized is not the hypothetical β-turanose of initial $[\alpha]_D$ approximately 71, predicted by theory. Nevertheless, the theory may be correct; if such is the case the hypothetical sugar must have a different ring structure from that of the known form. Such a result would not be surprising because by analogy with the structure of sucrose, the fructose constituent of which apparently possesses a 2,4-ring that shifts to the 2,5-position after the hydrolysis,[9] the fructose constituent of melezitose would be expected to possess the same 2,4-labile ring which could conceivably change to another type in crystalline turanose. It will apparently require new experimental evidence before this phase of the considerations can be further advanced and it is mentioned that the studies of Bridel and Aagaard on the hydrolysis of melezitose and turanose by various enzyme preparations lead them to doubt that sucrose is a constituent of the melezitose molecule. The writers are continuing the investigation of turanose; one (E. P.) will publish soon the description of several acyl derivatives of it which he has prepared and the other (C. S. H.) is studying its behavior in the Lobry de Bruyn alkaline rearrangement in the hope of converting it to a disaccharide aldose.

The Preparation of Crystalline Turanose from **Melezitose.**—The one-stage acid hydrolysis of melezitose must be carefully controlled for a good yield of turanose. Bridel and Aagaard recommend heating a solution containing 10% melezitose and 0.6% sulfuric acid for one and three-quarters hours on the water-bath but our results indicate that the hydrolysis proceeds under these conditions much beyond the first stage. The rotations of test samples of such a solution which were kept definitely at 100° for different lengths of time and then cooled, indicated that the first stage of hydrolysis is complete at this temperature in fifteen minutes. Three hundred grams of pure melezitose was dissolved in 2800 cc. of boiling water and a hot mixture of 19.2 g. of concentrated sulfuric acid (95%) and 150 cc. of water was added in one portion. The solution was kept boiling gently for fifteen minutes and was then cooled rapidly to room temperature and neutralized with an excess (22 g.) of calcium carbonate. About 10 g. of baker's yeast was then added to the unfiltered solution and fermentation was allowed to proceed at 40° for thirty-six to forty-eight hours, when it appeared to have nearly ceased. The solution was filtered after adding decolorizing carbon and the filtrate was concentrated under reduced pressure to a thick sirup, which was taken up with 500 cc. of

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[9] Hudson, THIS JOURNAL, 52, 1717 (1930).

absolute methyl alcohol and filtered from the insoluble calcium salts, using decolorizing carbon again. On nucleation of the solution with crystals of turanose it crystallized rapidly and became a solid mass after twenty-four hours at room temperature. The crystals were washed with absolute methyl alcohol and dried in a desiccator; yield, 110–125 g., and a further crop of 35–40 g. was obtainable from the mother liquor by reconcentration to a sirup and taking this up as before. Even the second mother liquor yielded a crop of 8–12 g. by removal of the methyl alcohol, solution of the residue in water, fermentation and retreatment by the usual procedure. The highest yield from a batch of 300 g. of melezitose was 178 g. or 87% of the theoretical, the lowest 80%. The sugar was recrystallized from boiling methyl alcohol and refluxing is advisable for obtaining a concentrated solution.

The separation of glucose from turanose, which is accomplished in the preceding directions through fermentation, may also be made by oxidizing the hexose with bromine water, which leaves the turanose largely unchanged, and precipitating calcium gluconate by the addition of alcohol.[10] One hundred grams of melezitose was hydrolyzed as directed and the cooled solution was neutralized with 11 g. of barium carbonate. Without filtration there was added a solution of 78 g. of barium benzoate in 1800 cc. of water followed by 10.2 cc. of bromine, which rapidly dissolved on stirring. After twelve hours the excess bromine was blown out, the barium was removed as sulfate and the main portion of the hydrobromic acid as lead bromide (using litharge to neutrality for congo red), and the final part as silver bromide. Excess heavy metals were then precipitated as sulfides. Dissolved benzoic acid was largely removed by several extractions with chloroform. The resulting colorless solution contained little besides turanose and gluconic acid. It was kept slightly alkaline to phenolphthalein with milk of lime for one hour at room temperature and then neutralized with sulfuric acid, filtered and concentrated to 500 cc. under reduced pressure. This solution was made slightly alkaline with lime and 450 cc. of 95% alcohol was added, followed by filtration and nucleation with calcium gluconate crystals. After standing overnight in the ice chest the salt was filtered off, 300 cc. of 95% alcohol was added and the filtration repeated. The filtrate was concentrated under reduced pressure to a thick sirup, which was dissolved in 400 cc. of cold methyl alcohol. A slight quantity of calcium gluconate soon separated but the filtrate gave no further precipitate on adding methyl alcohol. The solution was then concentrated to a thin sirup, which was seeded with turanose crystals; after a day it had become solid and yielded 44 g. of turanose. A second crop of 7.5 g. was obtained from the mother liquor, bringing the yield to 80% of the theoretical. The fermentation procedure is less laborious than the oxidation method but the latter may be used if difficulties arise in connection with the control of the growth of the yeast, as is sometimes the case.

Turanose crystallizes from methyl alcohol without solvent of crystallization and its analysis corresponds to the formula $C_{12}H_{22}O_{11}$. After drying at room temperature over calcium chloride in a vacuum desiccator to constant weight it lost no further weight when heated for two-hour intervals at 77, 98 and 110°, respectively, under reduced pressure. Micro combustions of samples weighing 2–3 milligrams showed C, 42.09, 42.17, 42.10; H, 6.38, 6.58, 6.56%; calculated for $C_{12}H_{22}O_{11}$: C, 42.08; H, 6.48. The combustions were made by Dr. R. T. K. Cornwell, to whom our thanks are expressed.

One of the authors (E. P.) expresses his thanks to the International Education Board for the grant of a fellowship which made possible his participation in this research.

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[10] Montgomery and Hudson, THIS JOURNAL, 52, 2101 (1930).

Summary

After several years' standing a sirupy preparation of turanose crystallized spontaneously and by nucleation with these crystals it has been possible to obtain rapid crystallization of large quantities of turanose. Directions for the preparation of the sugar in good yield from melezitose are given and some of its properties are recorded. Turanose shows a large and rapid mutarotation. A discussion of the structures of turanose and melezitose, in so far as present evidence permits, is presented.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

SALTS OF NITRILES. IV. SODIUM ALPHA-PHENYLBUTYRONITRILE[1,2]

BY MARY M. RISING AND EDMUND WARING LOWE

RECEIVED FEBRUARY 25, 1930 PUBLISHED JUNE 6, 1930

Previous reports[3] have described the preparation of the sodium and potassium salts of certain nitriles, and presented evidence for the nitride–carbide tautomerism of the anions of the salts, e. g.,

$$[C_6H_5C(R){=}C{=}N^-]Me^+ \rightleftarrows [C_6H_5C^-(R)CN]Me^+ \qquad (1)$$

Rising and Braun[3] made a quantitative study of the course of the reaction of phenylacetonitrile with sodium, and of the chemical behavior of the salt sodium phenylacetonitrile, $[C_6H_5CHCN]Na$. The present authors have studied quantitatively the analogous reaction of α-phenylbutyronitrile with sodium. They have found that the course of the reaction may be summarized in the equation

$$2C_6H_5C(C_2H_5)HCN + 2Na \longrightarrow [C_6H_5C(C_2H_5){=}C{=}N]Na + NaCN + C_6H_5C_3H_7 \qquad (2)$$

The hydrogen formed in the reaction of sodium with the nitrile reduces part of the salt to toluene and sodium cyanide

$$2C_6H_5C(C_2H_5)HCN + 2Na \longrightarrow 2[C_6H_5C(C_2H_5){=}C{=}N]Na + 2H \qquad (3)$$

$$[C_6H_5C(C_2H_5){=}C{=}N]Na + 2H \longrightarrow C_6H_5C_3H_7 + NaCN \qquad (4)$$

This reaction corresponds to that observed by Rising and Braun with sodium phenylacetonitrile, which is reduced by hydrogen to toluene and sodium cyanide. There are described also herein the conditions used for the preparation of the salts sodium and potassium α-phenylbutyronitrile. A study of the behavior of sodium α-phenylbutyronitrile has

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[1] The work here reported forms part of the dissertation of E. W. Lowe, to be presented in partial fulfilment of requirements for the doctorate degree at the University of Chicago.

[2] Original manuscript received August 31, 1929.

[3] Rising and Zee, THIS JOURNAL, (a) 49, 541 (1927) and (b) 50, 1699 (1928); Rising, Muskat and Lowe, *ibid.*, 51, 262 (1929); Rising and Braun, *ibid.*, 52, 1069 (1930).

brought to light a number of important facts. (1) The solid salt is extremely unstable and is obtainable only in an inert atmosphere, such as nitrogen. When exposed to air it bursts into flame. (2) The salt is somewhat unstable even in ether solution and decomposes very slowly, with the formation of sodium cyanide. This is believed to be a reaction of the nitride tautomer

$$[C_6H_5C(C_2H_5){=}C{=}N^-]Na^+ \longrightarrow NaN{=}C + C_6H_5C(C_2H_5) \qquad (5)$$

The instability of the salt makes the preparation of the pure compound extremely difficult to accomplish. This is unquestionably the chief cause of the earlier difficulties experienced in duplicating the work of Dr. Zee.[4] (3) Finally, it has been shown that ethylation of sodium a-phenylbutyronitrile produces a-phenyl-a-ethylbutyronitrile, $C_6H_5C(C_2H_5)_2CN$, in fairly good yield. This is probably a reaction of the carbide salt, since the product is a C-alkyl derivative

$$[C_6H_5C^-(C_2H_5)CN]Na^+ + C_2H_5I \longrightarrow C_6H_5C(C_2H_5)_2CN + NaI \qquad (6)$$

Silver and mercury salts of the nitrile are expected to yield N-alkylated derivatives, in part at least, and are being studied.

Experimental Part

1. Preparation of Sodium a-Phenylbutyronitrile in Ether Solution.—The apparatus used for the preparation of the salt was similar to that devised by Braun (Diagram, Ref. 3) for the reaction of phenylacetonitrile with sodium. Air and moisture were at all times rigorously excluded from this apparatus, an atmosphere of nitrogen being used for the reaction and for all operations in which sodium a-phenylbutyronitrile in solution or in solid form was handled. a-Phenylbutyronitrile of boiling point 110.5–111° at 11 mm., and n_D^{20} 1.5094[5] (pure α-phenylbutyronitrile n_D^{20} 1.5092) was used, prepared by the method of Bodroux and Taboury.[6] For the preparation of sodium a-phenylbutyronitrile, sodium dust (10 g., a 26% excess) was prepared in dry xylene as usual. After removal of the xylene, the sodium was covered with 250 cc. of dry ether, the ether was brought to boiling and the nitrile (50 g.) was dropped slowly into the reaction flask during the course of five hours; the reaction mixture was then refluxed for one and one-half hours more. As the reaction progressed sodium cyanide was precipitated and the ether solution became bright yellow. The reaction which occurred is expressed in Equation 2. After separation of the ether solution from the sodium cyanide by filtration, the filtrate F was made up to 400 cc. with ether and 50 cc. of it was used for the isolation of sodium a-phenylbutyronitrile for analysis. The rest of the filtrate containing the salt in ether solution was reserved for treatment with ethyl iodide to convert the salt into a-phenyl-a-ethylbutyronitrile.

2. Isolation of Sodium a-Phenylbutyronitrile, $[(C_6H_5)C(C_2H_5){=}C{=}N^-]Na^+$ and $[(C_6H_5)C^-(C_2H_5)CN]Na^+$.—A 50-cc. portion of filtrate F was allowed to flow into 2 liters of low-boiling ligroin, whereupon sodium a-phenylbutyronitrile was precipitated as a finely divided, pale yellow solid.—The salt was separated from the ether–ligroin mixture and analyzed, air being rigorously excluded in all operations.

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[4] See footnote, THIS JOURNAL, 50, 1699 (1928).

[5] Measurements of indices of refraction were made with an Abbé refractometer.

[6] Bodroux and Taboury, Bull. *soc. chim.*, [7] 4,666 (1910).

Anal. Subs., 0.2405, 0.2956: Na_2SO_4, 0.1235, 0.1510. Calcd. for $C_{10}H_{10}NNa$: Na, 13.70. Found: Na, 16.64, 16.55.

The high sodium content suggested that some decomposition of the salt into sodium cyanide had occurred during its preparation, a suspicion which was later confirmed, as will presently be shown. When the preparation of the salt was carried out more rapidly, this difficulty was largely overcome. It was found best also to concentrate the original ether solution of the salt to a volume of 175–200 cc. during its filtration from sodium cyanide. After filtration about half of this volume was allowed to flow into 5 liters of low-boiling ligroin. The ligroin and ether were then drawn off as rapidly as possible (with the loss of a considerable part of the salt, which was carried away with the solution). Analysis of the salt showed it to be pure.

Anal. Subs., 0.6143, 0.3267: Na_2SO_4, 0.2581, 0.1380. Calcd. for $C_{10}H_{10}NNa$: Na, 13.70. Found: Na, 13.60, 13.68.

Solid sodium a-phenylbutyronitrile was found to be exceedingly unstable; when exposed to air it smokes and bursts into flame. In ether solution the salt decomposes slowly with the formation of sodium cyanide.

3. Ethylation of Sodium α-Phenylbutyronitrile.—The remainder of filtrate F (350 cc.) containing sodium a-phenylbutyronitrile was treated with ethyl iodide (25 g.) during the course of several hours. The procedure followed was that used by Braun for the analogous reaction of sodium phenylacetonitrile with ethyl iodide. Equation 6 expresses the reaction which occurred. At the end of the reaction sodium iodide and traces of sodium cyanide (see Section 4) were removed from the reaction mixture by extraction with water. The ether solution remaining was then dried and the ether removed by evaporation. The residue of oil was fractionated at 13 mm.

FRACTION 1.—B. p. 57.5–65°, 14 g., propylbenzene, formed in the reaction of α-phenylbutponitrile with sodium (Equation 2).

Anal. Subs., 0.2924, 0.3098: CO_2, 0.9648, 1.0190; H_2O, 0.2640, 0.2771. Calcd. for C_9H_{12}: C, 89.92; H, 10.08. Found: C, 89.78, 89.96; H, 10.10, 10.04.

FRACTION 2.—B. p. 65–110°, 1–2 g., a mixture.

FRACTION 3.—B. p. 110–115°, 3.5 g., unchanged a-phenylbutyronitrile.

FRACTION 4.—B. p. 115–118°, 15 g , a-phenyl-a-ethylbutyronitrile.

Anal. Subs., 0.3130, 0.4832: N, 23.00 cc. (20°, 749 mm.), 35.04 cc. (20°, 749 mm.) (over 50% KOH). Subs., 0.3783, 0.3366: CO_2, 1.1503, 1.0240; H_2O, 0.2953, 0.2647. Calcd. for $C_{12}H_{15}N$: N, 8.09; C, 83.17; H, 8.73. Found: N, 8.28, 8.17; C, 82.93, 82.97; H, 8.76, 8.80.

FRACTION 5.—B. p. 118–195°, 1–2 g., not identified.

FRACTION 6.—Decomposes above 195°; a gummy solid.

4. Determination of Sodium Cyanide.—Sodium cyanide is formed (a) as one of the products of the reaction of a-phenylbutyronitrile with sodium (Equation 2), and (b) by the slow decomposition of sodium a-phenylbutyronitrile itself in ether solution. The cyanide (a) formed by and during the action of sodium on the nitrile was collected on the filter of the reaction apparatus.? The amount formed was determined by the Liebig method,[8] and found to be 8.1 g. A further formation of sodium cyanide (b) in filtrate F was observed. This solution, originally clear, slowly deposited a small quantity of a colorless salt which was suspected to be sodium cyanide. The amount of cyanide thus formed was determined in a number of instances. (1) Filtrate F obtained from 50 g. of nitrile and 10 g. of sodium was allowed to stand for forty hours. A

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[7] See Diagram, Rising and Braun, Ref. 3.

[8] Liebig, *Ann.*, 77, 102 (1851).

white precipitate of sodium cyanide was deposited, in amount 0.744 g., determined by the Liebig method. (2) Filtrate F obtained from 20 g. of nitrile and 5.9 g. of sodium was allowed to stand for five days. A precipitate was formed as in (1). Ethylation of the nitrile salt in the solution was then carried out, and the amount of cyanide formed during the five days and the time of ethylation was determined by analysis for cyanide of the aqueous extract of the ethylation reaction mixture; total cyanide, 0.0986 g. (3) Ethylation of filtrate F obtained from 50 g. of nitrile and 10 g. of sodium was carried out as usual. Total cyanide, determined as in (2), was found to be 0.176 g. Clearly, sodium α-phenylbutyronitrile has a tendency to decompose slowly in its ether solution. The conditions which cause, or favor, this change are not as yet understood, nor has any product of the decomposition, aside from sodium cyanide, been isolated. The decomposition may be a reaction of the nitride salt (Equation 5).

5. Quantitative Summary of the Course of the Reaction of a-Phenylbutyronitrile with Sodium.—There follows a list of products formed in the reaction of 50 g. of nitrile with 10 g. of sodium, together with the yields obtained, calculated on the basis of Equations 2 and 6 (correction is made for the recovered α-phenylbutyronitrile).

(a) Recovered a-phenylbutyronitrile: 4 g., or 8%.

(b) Propylbenzene: 16 g., or 84.2% of the calculated amount.

(c) Sodium cyanide: 8.1 g., or 95.6% of the calculated amount. This quantity includes that formed in the reaction expressed in Equation 2, and, in addition, any traces of cyanide formed by the slow decomposition of a-phenylbutyronitrile up to the time of filtration.

(d) Sodium α-phenylbutyronitrile: since the yield of this product cannot be determined directly owing to the instability of the salt in solid form, the yield of its ethylation product may be taken as a fairly accurate measure of the amount of salt formed; yield of α-phenyl-α-ethylbutyronitrile, 17.1 g., or 62.4% of the calculated amount.

6. Potassium **α-Phenylbutyronitrile,** $[(C_6H_5)C(C_2H_5){=}C{=}N^-]K^+$ and $[(C_6H_5)C^-(C_2H_5)CN]K^+$.—The potassium salt was prepared by a procedure resembling that used for the preparation of sodium α-phenylbutyronitrile. The potassium salt obtained contained 20.80 and 20.67% of potassium (calculated potassium is 21.34%). The salt is a pale yellow, unstable substance which decomposes rapidly on exposure to air.

Summary

1. The reaction of a-phenylbutyronitrile with sodium has been studied quantitatively and the course of the reaction established.

2. Sodium a-phenylbutyronitrile and the analogous potassium salt have been prepared and isolated by a method similar to that developed by Rising and Braun for obtaining sodium a-phenylbutyronitrile.

3. Sodium a-phenylbutyronitrile decomposes slowly in ether solution into sodium cyanide.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

MERCURATED AZO DYES DERIVED FROM BENZIDINE AND ORTHO-TOLIDINE

BY EDWARD McMAHON AND C. S. MARVEL

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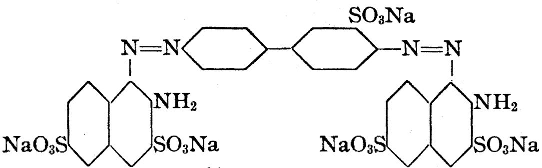
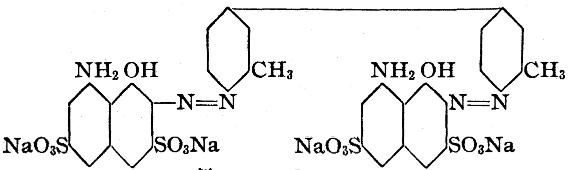
Certain azo dyes, particularly Trypan Red and Trypan Blue, have been reported[1] as having some trypanocidal action. These dyes were obtained by tetrazotizing certain benzidine derivatives and coupling with naphthalene derivatives having sulfonic acid groups in the 3- and 6-positions. The structures for these two dyes are indicated by the formulas



Trypan Red



Trypan Blue

The use of organic mercury compounds has also met with some success in the treatment of diseases which are caused by trypanosomes. Since mercury can usually be introduced into aromatic amines, it seemed worth while to prepare some mercurated benzidine derivatives and use these to obtain dyes related to Trypan Red and Trypan Blue. Such products might be expected to have very useful pharmacological properties.

Raiziss[2] has mentioned that acetoxymercuri-benzidine can be obtained as a white amorphous powder by boiling benzidine and mercuric acetate in dilute hydrochloric acid. He has never described this procedure in detail and has given no further information concerning the compound. Bernardi and Tartarini[3] have treated benzidine with mercuric acetate in glacial acetic acid and have obtained a very unstable compound which melted with decomposition at 138–140°. They say that the compound is too unstable for analysis, but suggest that it has the structure, $H_2N(p\text{-}NH_2C_6H_4)\text{-}C_6H_3HgOCOCH_3$.

In repeating this work it has been found possible to introduce one acet-

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[1] Ehrlich, *Berl. klin. Wochschr.*, *44*, 235 (1907).

[2] Raiziss in "Organic Compounds of Mercury," by F. C. Whitmore, The Chemical Catalog Company, Inc., New York, 1921, p. 349.

[3] Bernardi and Tartarini, Gazz. *chim. ital.*, *57*, 223 (1927).

sxymercuri group into benzidine with considerable ease. The compound which was obtained melted somewhat higher (144–146°) than was recorded by Bernardi and Tartarini for their product. The product always contained acetic acid of crystallization and when this was removed by heating the sample, decomposition resulted. Only one acetoxymercuri group could be introduced even when benzidine was treated with two or three equivalents of mercuric acetate. The new mercury compound was quite unstable and lost its mercury when suspended in water. The mercury atom was attached to the benzene ring since the mercurated amine could be tetrazotized and coupled to give azo dyes which contained the expected amount of mercury.

o-Tolidine was also mercurated and the derivative was very similar to the benzidine derivative in its properties. On account of the instability of these products their exact structure has not been established. The acetoxymercuri group is presumably ortho to one of the amino groups.

In preparing the tetrazonium salts from acetoxymercuri-benzidine and acetoxymercuri-o-tolidine it was necessary to treat an absolute alcoholic suspension of the amine with n-butyl nitrite in the presence of a little aqueous hydrochloric acid. When the reaction was attempted in water suspension, the mercury was removed from the molecule. The coupling reactions were also carried out in absolute alcohol suspension. Three dyes were prepared and analyzed. Acetoxymercuri-benzidine was tetrazotized and coupled with 2-amino-8-naphthol-6-sulfonic acid and with 1-amino-8-naphthol-3,6-disulfonic acid (H-acid). Acetoxymercuri-o-tolidine was tetrazotized and coupled with H-acid. The dyes thus obtained separated with alcohol of crystallization. Attempts further to purify the dyes were not successful due to their instability. When dissolved in water containing sodium bicarbonate, the dyes lost metallic mercury in a few days. Heating the water solutions caused decomposition very quickly. The instability of the dyes made them unsuitable for pharmacological tests.

Experimental Part

Acetoxymercuri-benzidine.—In a liter beaker equipped with a mechanical stirrer was placed a solution of 31.8 g. (0.1 mole) of mercuric acetate in 150 cc. of glacial acetic acid. The stirrer was started and a solution of 18.4 g. (0.1 mole) of benzidine in 300 cc. of glacial acetic acid was added slowly. A precipitate began to appear at once. The mixture was stirred for about ten minutes after the solutions were mixed and was then filtered. The precipitate was washed first with glacial acetic acid, and then with ether and finally dried in the air in the dark. The yield was 55 g. of a product which melted at 144–146° with decomposition.

This compound was insoluble in water, alcohol, ether and benzene. It turned gray on standing in the light. The water suspension was acid to litmus. When this suspension was heated the compound darkened rapidly. An aqueous suspension of the product reacted in the cold with sodium sulfide solution giving mercuric sulfide. Aqueous hydrochloric acid removed the mercury from the compound very rapidly. The same product was obtained when the preparation was repeated using 63.6 g. and 95.4 g. of mercuric acetate with 18.4 g. of benzidine.

A complete analysis of this mercurated benzidine was made. Carbon and hydrogen were determined by combustion. Mercury was determined by Whitmore's gold crucible method.[4] Nitrogen was determined by the Kjeldahl method. Acetic acid was determined by drying a sample under reduced pressure over solid sodium hydroxide and by direct titration of a sample with standard alkali.

Anal. Subs., 0.1855, 0.1718: CO_2, 0.2650, 0.2440; H_2O, 0.0726, 0.0669. Subs., 0.1000, 0.1000; Hg, 0.0320, 0.0325. Subs., 1.000, 1.000: cc. of 0.102 *N* H_2SO_4, 32.00, 31.00. Subs., 0.5000; loss in weight on drying, 0.0535. Subs., 0.2000; cc. of 0.0980 N NaOH, 12.2. Calcd. for $C_{14}H_{14}N_2O_2Hg{\cdot}3CH_3COOH$: C, 38.8; H, 4.2; Hg, 32.5; N, 4.5; CH_3COOH, 9.65; neutral equivalent, 207. Found: C, 39.0, 38.8; H, 4.3, 4.3; Hg, 32.0, 32.5; N, 4.52, 4.43; CH_3COOH, 10.07; neutral equivalent, 204.

Acetoxymercuri-o-tolidine.—This compound was obtained in the same manner as described for the benzidine derivative using 21.2 g. of o-tolidine in place of the equivalent amount of benzidine. The yield was 52 g. of a product which melted with decomposition at 120". In all of its other properties it was very similar to the benzidine derivative.

Anal. Subs., 0.1500: Hg, 0.0500. Calcd for $C_{16}H_{18}N_2O_2Hg{\cdot}2CH_3COOH$: Hg, 33.9. Found: Hg, 33.3.

Tetrazotization of **Acetoxymercuri-benzidine and** Coupling with H-Acid.—To *a* suspension of 6.2 g. of acetoxymercuri-benzidine in 300 cc. of absolute alcohol was added 1.5 cc. of concentrated hydrochloric acid. The mixture was cooled to 0° and then with continuous stirring 2.1 g. of n-butyl nitrite was added. Stirring was continued for ten minutes and then this mixture was added to a cold suspension of 6.4 g. of H-acid in 300 cc. of absolute alcohol to which had been added about 0.5 cc. of concentrated hydrochloric acid. The mixture was stirred in the cold for about thirty minutes and then allowed to come to room temperature. The dye separated as a red-brown crystalline compound. The product was collected on a suction filter, washed with alcohol and ether and dried in the air out of direct light. The dye was insoluble in water. It dissolved in aqueous sodium bicarbonate to give a purple solution. The alkaline solution deposited free mercury within forty-eight hours. Since the dye was too unstable to purify, it was analyzed directly. Nitrogen was determined by the Dumas method, sulfur in the Parr bomb, mercury by the gold crucible method and sodium as the sulfate by decomposition with nitric and sulfuric acids. Ethyl alcohol was present as alcohol of crystallization. This was demonstrated by drying the sample to constant weight in a vacuum dryer over calcium chloride.

Anal. Subs., 0.1354: 9.95 cc. of N_2 at 33° and 750 mm. Subs., 0.5000, 0.5000: $BaSO_4$, 0.3752, 0.3831. Subs., 0.1500, 0.1500: Hg, 0.0245, 0.0245. Subs., 0.2965, 0.2222: Na_2SO_4, 0.0335, 0.0270. Subs., 0.2188: C_2H_5OH lost in drying, 0.0163. Calcd. for $C_{34}H_{24}O_{16}N_6S_4HgNa_2{\cdot}2C_2H_5OH$: N, 6.5; S, 10.3; Hg, 16.2; Na, 3.7; C_2H_5OH, 7.4. Found: N, 7.6; S, 10.3, 10.5; Hg, 16.3, 16.3; Na, 3.8, **3.9;** C_2H_5OH, 7.6.

Tetrazotization of Acetoxymercuri-*o*-tolidine and Coupling **with** H-Acid.—To **a** suspension of 6.2 g. of acetoxymercuri-o-tolidine in 300 cc. of absolute ethyl alcohol was added 1.5 cc. of concentrated hydrochloric acid. The mixture was cooled to 0°; then while stirring there was added 2.1 g. of butyl nitrite. Sitrring was continued for ten minutes and then this mixture was added to a cold suspension of 6.4 g. of H-Acid in 300 cc. of absolute alcohol. The mixture was stirred in the cold for thirty minutes

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[4] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co. Inc., New York, 1921, p. 365.

and then allowed to come to room temperature. The orange-colored powder which separated was collected on a suction filter and washed with alcohol and ether. The product was dried in the air out of direct light. This dye was only slightly soluble in water, but in sodium bicarbonate solution it gave a deep purple solution. Mercury separated from this solution on standing for forty-eight hours.

Anal. Subs., 0.1500: Hg, 0.0217. Calcd. for $C_{36}H_{28}O_{16}N_6S_4Na_2Hg\cdot 5C_2H_5OH$: Hg, 14.24. Found: Hg, 14.4.

Tetrazotization of Acetoxymercuri-benzidine and Coupling with 2-Amino-8-naphthol-6-sulfonic Acid.—The tetrazotization was performed with the same amount of material as described before and the tetrazonium salt was coupled with 4.8 g. of 2-amino-8-naphthol-6-sulfonic acid. The dye separated as a reddish-purple powder which was washed with alcohol and ether and dried in the air out of direct light. It was only slightly soluble in water, but gave a deep purple solution in sodium bicarbonate solution. This solution deposited mercury on standing for forty-eight hours.

Anal. Subs., 0.1500: Hg, 0.0276. Calcd. for $C_{34}H_{26}O_{10}N_6S_2Hg\cdot 3C_2H_5OH$: Hg, 18.5. Found: Hg, 18.4.

Summary

1. Monoacetoxymercuri derivatives have been prepared by treating benzidine and o-tolidine in glacial acetic acid with mercuric acetate.
2. These acetoxymercuri derivatives can be tetrazotized and coupled with naphthalene derivatives to give azo dyes which are related in their structure to Trypan Red and Trypan Blue.
3. The mercurated dyes are not stable and readily lose mercury and are hence unsuitable for pharmacological testing.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

ARYL SULFONE DERIVATIVES OF DIBASIC ACIDS[1]

BY THEODORE W. EVANS AND WILLIAM M. DEHN

RECEIVED MARCH 1, 1930 PUBLISHED JUNE 6, 1930

It was recently shown that phthalyl chloride reacts readily with sulfonamides to give phthalimide derivatives[2] when the materials are merely heated or are boiled in toluene solution. The following study develops this and other practical methods for the preparation of aryl sulfone derivatives of dibasic acids.

Whereas certain suggested methods such as heating phthalic anhydride with *p*-tolyl sulfonamide or with its sodium salt, or heating p-tolyl sulfonyl chloride with phthalimide, failed to yield the desired product, it was found that heating phthalic anhydride with p-tolyl sulfonamide in the presence of phosphorus oxychloride readily gave the phthalimide derivative in sub-

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[1] The material presented in this paper is from part of a thesis submitted by Theodore Evans, du Pont Fellow for 1929–1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1930.

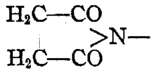
[2] Evans and Dehn, THIS JOURNAL, 51, 3651 (1929).

TABLE I

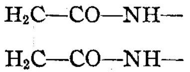
RESULTS OF EXPERIMENTS

Acid derivative[a]	Used Sulfonamide, etc.	Method	Formula of compound[b]	M. p., °C.	Crystal form	Soluble in hot solvent.	Sulfur, % Calcd.	Sulfur, % Found
SCl	Phenyl	I[c]	X—$SO_2 \cdot C_6H_5$	161	Prisms	Toluene	13.40	13.59
SCl	*p*-Bromphenyl	II	X—$SO_2 \cdot C_6H_4Br$(*p*)	181	Prisms	Toluene	10.08	10.16
SCl	p-Tolyl	II[d]	S—$SO_2 \cdot C_7H_7$(*p*)	184	Prisms	Alcohol	12.66	12 78
SA	p-Tolyl	III	X—$SO_2 \cdot C_7H_7$(*p*)	184	Prisms	Alcohol	12.66	12 74
SCl	*m*-Nitro-*p*-tolyl	II	X—$SO_2 \cdot C_7H_6NO_2$[d,f]	212–213	Prisms	Toluene	10.75	10 51
SCl	o-Tolyl	I, II	X—$SO_2C_7H_7$(O)	136	Prisms	Toluene	12.66	12.63
SCl	*β*-Naphthyl	I	X—$SO_2 \cdot C_{10}H_7$	175–176	Rectangles	Alcohol	11.08	10.97
SA	Phenyl	III	Y=$(SO_2C_6H_5)_2$	235–237	Prisms	MEK[g]	16.18	1569
SA	*p*-Bromphenyl	III	Y=$(SO_2C_6H_4Br)_2$	231	Needles	Toluene	11.57	11.43
SA	m-Nitro-p-tolyl	III	Y=$(SO_2C_7H_6NO_2)_2$	236	Needles	Toluene	12.47	12.47
SA	*o*-Tolyl	IV	Y=$(SO_2C_7H_7)_2$	231–232	Needles	MEK[g]	15.11	14.96
SCl	*o*-Tolyl	II	Y=$(SO_2C_7H_7)_2$	231–232	Needles	Alcohol	15.11	
SA	*β*-Naphthyl	III	Y=$(SO_2C_{10}H_7)_2$	248	Prisms	Insoluble	12.92	12.46
PA	Phenyl	III[f]	Z.$SO_2C_6H_5$	205	Needles	Toluene	11.12	11.09
PA	p-Bromophenyl	III	Z.$SO_2C_6H_4Br$	246	Needles	Toluene	8.76	
PCl	*p*-Bromophenyl	II	Z.$SO_2C_6H_4Br$	246	Needles	Toluene	8.76	8.65
PA	p-Tolyl	III[f]	Z.$SO_2C_7H_7$	237[d]	Prisms	Toluene	10.59	10.42
PA	m-Nitro-p-tolyl	III[f]	Z.$SO_2C_7H_6NO_2$	247	Needles	Toluene	9.26	
PA	*o*-Tolyl	III[f]	Z.$SO_2C_7H_7$	182[d]	Prisms	Toluene	10.59	10.07
PCl	*β*-Naphthyl	I	Z.$SO_2 \cdot C_{10}H_7$	216	Prisms	Toluene	9.51	9.23
PA	*β*-Naphthyl	IV	Z.$SO_2.C_{10}H_7$	216	Prisms	Toluene	9.51	9.44
SCl	Benzamide	II[e]	X—$CO \cdot C_6H_5$	130	Hexagons	EtOH		
Maleic acid	Phenyl	111	$C_4H_2O_2(NHSO_2C_6H_5)_2$	258	Prisms	Insoluble	16.26	15.75

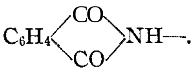
[a] Abbreviations used: SA = succinic anhydride; SCl = succinyl chloride; PCl = phthalyl chloride; PA = phthalic anhydride.

[b] X = 

$$\begin{matrix} H_2C—CO \\ | \quad\quad\quad >N— \\ H_2C—CO \end{matrix}$$

Y = 

$$\begin{matrix} H_2C—CO—NH— \\ | \\ H_2C—CO—NH— \end{matrix}$$

Z = 

$$C_6H_4\left\langle\begin{matrix} CO \\ CO \end{matrix}\right\rangle NH—.$$

[c] Gerhardt and Chiozza, ***Ann.** chim.*, [3] 46, 158 (1856), heated the materials to 160°; melting point given, 160°. [d] Walkowa, J. Russ. *Phys.-Chem. Soc.*, 2, 244 (1870); no melting point given. [e] Titherley prepared this compound by the action of benzoyl chloride on succinimide; melting point given, 130°. [f] Evans and Dehn, THIS JOURNAL, 51, 3651 (1929). [g] Methyl ethyl ketone.

stantially quantitative yield. This method was tried with various aryl sulfonamides and was found to be uniformly effective with phthalic anhydride. The same method applied to succinic and maleic anhydrides yielded compounds of the type $(H_2CCO\text{-}NHSO_2R)_2$, except that when R is p-tolyl the succinimide derivative results. However, with succinyl chloride the amides give succinimide derivatives. That the succinyl chloride does react in the normal form is evidenced by its reaction with benzamide to give benzoyl succinimide,[3] with *p*-tolyl sulfonamide to give the same product as the anhydride, and with o-tnlyl sulfonamide to give in part the succinamide derivative.

It seems probable that with anhydrides and phosphorus oxychloride reactions take place in two steps, the first being the conibination of one molecule of anhydride and one molecule of amide, $HOOCCH_2CH_2CONHSO_2R$. This then either forms the imide derivative or eliminates water with a second molecule of the amide to form the di-substituted diamide.

Methods of Preparation

I. The reacting materials were heated without a solvent in an oil-bath to 150–200°. The product was then recrystallized, usually from toluene.

II. The materials were refluxed in toluene for twelve to twenty-four hours. The solution was then concentrated, precipitated by the addition of ether, and the product filtered off and recrystallized.

III. The materials were heated to 100° in phosphorus oxychloride for several hours. Ether was then added, the product filtered off and washed well with ether and hot alcohol, and then recrystallized.

IV. The same as III except that the materials were heated to the boiling point of the phosphorus oxychloride.

Summary

1. Phthalyl and succinyl chlorides react with sulfonamides to give imide derivatives.

2. Phthalic anhydride reacts with sulfonamides in the presence of phosphorus oxychloride to give substituted phthalimides.

3. Succinic anhydride reacts with sulfonamides in the presence of phosphorus oxychloride to give derivatives of succinamide except in the case of *p*-tolyl sulfonamide.

4. Maleic anhydride and benzene sulfonamide in the presence of phosphorus oxychloride give the derivative of maleic amide.

SEATTLE, WASHINGTON

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[3] *Although benzoyl succinimide and benzamide melt within one degree of each other, there can be no doubt that our product is benzoyl succinimide, since it is insoluble in ether, whereas benzamide is very soluble, and, further, when cautiously hydrolyzed with sodium carbonate, it yields benzoyl succinamic acid,* m. p. 180° [*Titherley, J. Chem. Soc.,* **85**, 1679 (1904)].

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXX. THE ALPHA AND BETA METHYL-d-GALACTOSIDES AND THEIR TETRA-ACETATES[1]

BY J. K. DALE AND C. S. HUDSON

RECEIVED MARCH 6, 1930 PUBLISHED JUNE 6, 1930

In 1918 the writers[2] prepared the crystalline tetra-acetate of α-methyl-*d*-galactoside for the first time and found its rotation to agree with the value that was predicted by the rules of isorotation. By an oversight the details of the preparation were not published and mention was not made that the substance was new; in consequence our record of the compound has been overlooked by later investigators, probably because it was not mentioned in recent reference books. Levene and Sobotka[3] attempted the preparation of this substance in 1926 but were unable to obtain it crystalline. They record $[\alpha]_D + 69.3$ in chloroform for a sirup which had been distilled at 190° under 0.8-mm. pressure. Using this figure in their calculations they concluded that the molecular rotation difference for the acetylated methylgalactosides did not agree with the corresponding difference for the acetylated methylglucosides and hence that optical superposition or isorotation does not hold among the acetylated methylglycosides. This conclusion does not appear justified, however, because the specific rotation which they record for their sirupy α-tetra-acetylmethylgalactoside is certainly not the value for the pure substance. We used the value $[\alpha]_D^{20} +133$ in our earlier article and now on repreparing this compound find this value to be correct for the pure substance, which we have obtained again in crystalline form without difficulty. We recorded a table in our 1918 article which clearly shows that isorotation holds closely for the alpha and beta acetates of methyl glucoside, xyloside and galactoside, all of which were prepared in pure crystalline condition. It has also been shown[4] that the rotations of the hepta-acetates of alpha and beta methylgentiobioside agree closely with values calculated from theory. The methylgalactosides and their acetates have now been carefully prepared again and the rotations have been found to agree closely with the previously published experimental values. The results are included in the following two tables, which are to be regarded as revisions and extensions of the two similar tables previously published.[2,5]

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[1] Publication authorized by the Director of the Bureau of Standards, U. S. Department of Commerce. No. XXIX was published in THIS JOURNAL, 52, 2519 (1930).

[2] Hudson and Dale, *ibid.*, 40, 997 (1918).

[3] Levene and Sobotka, J. *Biol. Chem.*, 67, 759, 771 (1926).

[4] Hudson and Johnson, THIS JOURNAL, 39, 1272 (1917); Hudson, *ibid.*, 47, 872 (1925); Helferich, Klein and Schafer, Ann., 447, 26 (1926).

[5] Hudson, THIS JOURNAL, 47, 268 (192.5).

Table I shows the specific rotation in water and molecular rotational difference for five pairs of methyl glycosides. The close agreement in the molecular rotational differences for the pairs is evidence that the rules of isorotation hold in first approximation, though not with mathematical exactness, for compounds of this type.

TABLE I

ROTATIONS IN WATER OF PURE METHYLGLYCOSIDES

Substance	Mol. wt.	$[\alpha]_D$	$[M]_D$	Difference
a-Methyl-d-glucoside[6]	194	158 9	30,830	37,460
β-Methyl-*d*-glucoside	194	−34.2	−6,630	
a-Methyl-d-galactoside	194	196.1	38,040	37,900
β-Methyl-*d*-galactoside	194	0.7	140	
α-Methyl-*d*-xyloside[5]	164	153.9	25,240	35,980
β-Methyl-*d*-xyloside	164	−65.5	−10,740	
α-Methyl-*l*-arabinoside[5]	164	17.3	2,840	−37,420
β-Methyl-*l*-arabinoside	164	245.5	40,260	
a-Methyl-gentiobioside[4]	356	65.5	23,300	36,100
β-Methyl-gentiobioside	356	−36	−12,800	

Table II shows the specific rotations in chloroform and molecular rotational differences for four pairs of acetylated glycosides. Here again there is a close agreement in the molecular rotational differences, leading to the conclusion that the rules of isorotation hold closely when applied to the completely acetylated glycosides. On the basis of these data we must disagree with Levene and Sobotka's conclusion that isorotation does not apply in the group of the known acetylated methylglycosides.

TABLE II

ROTATIONS IN CHLOROFORM OF ACETYLATED METHYLGLYCOSIDES

Substance	Mol. wt.	$[\alpha]_D$	$[M]_D$	Difference
a-Tri-acetyl-methyl-d-xylosidez	290	119.6	34,700	52,300
β-Tri-acetyl-methyl-*d*-xyloside	290	− 60.7	−17,600	
a-Tetra-acetyl-methyl-d-glucoside[2]	362	130.5	47,300	53,900
β-Tetra-acetyl-methyl-*d*-glucoside	362	−18.3	−6,600	
a-Tetra-acetyl-methyl-d-galactoside	362	133	48,400	53,460
β-Tetra-acetyl-methyl-*d*-galactoside	362	−14.0	−5,060	
a-Hepta-acetyl-methyl-gentiobioside[4]	660	64.5	41,900	54,250
β-Hepta-acetyl-methyl-gentiobioside	650	−19	−12,350	

Experimental Part

Preparation of Alpha and Beta Methyl-*d*-galactoside.—Fifty grams of d-galactose was refluxed on a steam-bath with 400 cc. of methanol containing 1% of hydrogen chloride until the rotation became constant, which required fourteen hours. A few pieces of porous plate in the flask insured steady boiling. After neutralizing the acid with silver carbonate and filtering, the filtrate was decolorized with active carbon and

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[6] Riiber. *Ber.*. **57**, 1797 (1924).

concentrated to a thick sirup under reduced pressure. This sirup was dissolved in 200 cc. of hot isopropyl alcohol, from which on cooling there crystallized 26 g. of a-methyl-d-galactoside monohydrate which showed $[\alpha]^{20}_{D}$ +175.5 in water. After one recrystallization from hot absolute alcohol the value was $[\alpha]^{20}_{D}$ +178.7 (0.7064 g. of substance in 25 cc. of aqueous solution rotated 10.1 to the right in a 2-dm. tube). The mother liquor was evaporated under reduced pressure until it crystallized spontaneously in the flask. The resulting mixture of sirup and crystals was dissolved in 100 cc. of hot isopropyl alcohol, from which on cooling there crystallized 9.2 g. of β-methyl-*d*-galactoside which showed [a]: +1.2 in water. After recrystallization from hot absolute alcohol the value was $[\alpha]^{20}_{D}$ +0.61 in aqueous solution (1.0261 g. of substance in 25 cc. of aqueous solution rotated 0.05" to the right in a 2-dm. tube).

Preparation of Alpha Tetra-acetyl-methyl-d-galactoside.—This compound was readily prepared by dissolving 13.5 g. of a-methyl-d-galactoside in a mixture of 68 cc. of acetic anhydride and 88 cc. of pyridine which had previously been cooled in an ice-bath. The mixture was kept in the ice-bath for three hours and then in an ice chest for two days. The solution was then poured into a liter beaker filled with crushed ice and crystallization took place almost immediately. After the ice had melted the crystalline material was separated from the ice water by filtration. Dried at 35° there was obtained 20 g. of substance. It was purified by recrystallization from a mixture of equal parts of ethyl ether and petroleum ether followed by a second recrystallization from 50% alcohol. After the first recrystallization $[\alpha]^{20}_{D} = +132.5°$. After the second recrystallization, $[\alpha]^{20}_{D} = +133.0$ (0.7209 g. of substance in 25 cc. of chloroform[7] solution rotated 7.67 to the right in a 2-dm. tube). A check determination of the specific rotation was made in chloroform which had been purified by shaking with five successive portions of water and drying with calcium chloride. The value was +133.1°, which is not sensibly different from the previous measurement.

The compound melted sharply at 87° (corr.). It crystallized from water, ether or a mixture of alcohol and petroleum ether, in radiating prismatic needles. It was readily soluble in ether, alcohol, chloroform, acetone and hot water, but insoluble in petroleum ether. An acetyl determination was made by Kunz's[8] method; 0.2598 g. of substance was dissolved in 25 cc. of pure acetone and 40 cc. of 0.1 *N* sodium hydroxide was added. After standing all night in an ice box the solution was titrated with 0.1 N hydrochloric acid and it was found that 28.62 cc. of the 0.1 N alkali had been neutralized, indicating 66.09% of acetic acid; calcd., 66.30%.

De-acetylation of Alpha-Tetra-acetyl-methyl-*d*-galactoside.—Thirteen grams of the twice recrystallized tetra-acetate was dissolved in 125 cc. of methanol saturated with dry ammonia gas. The solution was kept in an ice box overnight and then evaporated under diminished pressure almost to dryness. The residue was extracted with several portions of warm ether to remove acetamide and then dissolved in a little hot absolute alcohol. On cooling, crystals separated which were filtered from the mother liquor and washed with absolute alcohol. After recrystallization from absolute alcohol and drying at 35° the $[\alpha]^{20}_{D}$ of this product was found to be \$179.3 in aqueous solution (1.0052 g. of substance in 25 cc. of solution rotated 14.42 to the right in a 2-dm. tube). This agrees with the value, $[\alpha]^{20}_{D}$ +178.7, found for a-methyl-d-galactoside monohydrate made by direct methylation of d-galactose.

The water of crystallization was determined by drying a 1-g. sample in a weighing bottle to constant weight at 90° and 50 mm.; found: 8.47% of water; calculated for methylgalactoside monohydrate, 8.49%. This dried material was used for a direct

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[7] The specific rotation determinations of a- and β-tetra-acetyl-methylgalactoside were made in U. S. P. chloroform unless otherwise stated.

[8] Kunz and Hudson, THIS JOURNAL, 48, 1982 (1926).

determination of the specific rotation of anhydrous a-methyl-d-galactoside. The dried product, amounting to **0.9153** g., when dissolved in water to a volume of **25** cc. read **14.36** to the right in a 2-dm. tube, hence $[\alpha]^{20}_{D}$ +196.1, which corresponds to $[\alpha]^{20}_{D}$ +179 4 for the monohydrate, in good agreement with the directly observed values.

Preparation of **β-Tetra-acetyl-methyl-*d*-galactoside.**—Seven grams of recrystallized β-methyl-*d*-galactoside was acetylated by heating for three hours on a steam-bath with **16** cc. of acetic anhydride and 2 g. of fused sodium acetate. The reaction mixture was then poured into ice water. The sirupy phase which separated crystallized on standing overnight in an ice box. **A** further portion was obtained by neutralizing the supernatant acid water with sodium bicarbonate and extracting with chloroform. The chloroform extract was dried with calcium chloride and evaporated to a thin sirup which on stirring with the addition of petroleum ether crystallized immediately. The two portions of impure β-tetra-acetyl-methyl-*d*-galactoside were combined and recrystallized from absolute alcohol. The yield of pure product was 8 g. or 61% of the theoretical. It showed $[\alpha]^{20}_{D}$ **−14.05** in chloroform **(0.5514** g. of substance in **25** cc. of chloroform solution rotated **0.62** to the left in a 2-dm. tube). After a second recrystallization from absolute alcohol the specific rotation was unchanged.

De-acetylation of **β-Tetra-acetyl-methyl-*d*-galactoside.**—As a check upon the specific rotation and purity of the β-methyl-*d*-galactoside that was obtained by the direct methylation of d-galactose, the substance was also prepared by de-acetylating the purified β-tetra-acetyl-methyl-*d*-galactoside described above. Four grams were dissolved in 40 cc. of methanol saturated with dry ammonia gas and the solution kept in an ice box overnight. It was then evaporated until on reaching the consistency of a thin sirup β-methylgalactoside crystallized in the flask. The crystalline mass was extracted with several portions of warm ether to remove acetamide and was then dissolved in hot absolute alcohol. On cooling β-methylgalactoside quickly crystallized. After filtering, washing with absolute alcohol and drying at 35°, there was obtained 2.0 g. or 93% of the theoretical. It showed $[\alpha]^{20}_{D}$ **0.73**" in aqueous solution **(1.0194** g. of substance in **25** cc. of aqueous solution rotated 0.06° to the right in a 2-dm. tube), in good agreement with the previous measurement.

Summary

The preparation and properties of pure crystalline α-methyl-*d*-galactoside tetra-acetate are described. The rotation of the substance was recorded by us in 1918 but the details of preparation were inadvertently omitted. These are now supplied and our earlier measurement of the rotation is confirmed. Using the best revised data for the rotations of the pure alpha and beta forms of methylxyloside, arabinoside, glucoside, galactoside and gentiobioside, and such of the fully acetylated derivatives of these substances as are known, it is shown by the data recorded in Tables I and II that the rules of isorotation hold closely in all these cases.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

CHALCONES. II. DECOMPOSITION BY ALKALI

BY R. L. SHRINER AND T. KUROSAWA

RECEIVED MARCH 7, 1930 PUBLISHED JUNE 6, 1930

Certain of the natural yellow and orange coloring matters are substituted benzalacetophenone derivatives called chalcones. The structure of these chalcones is usually determined by decomposing them with alkali and isolating and identifying the products. The degradation products however, depend on the condition used for splitting the chalcone.

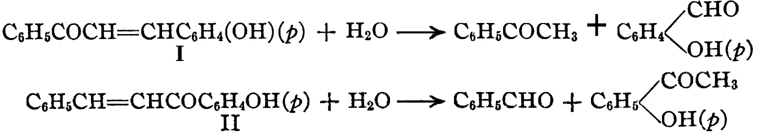
The chalcone from hyssopin was shown by synthesis to be 2,4,6-trihydroxystyryl-3,4-methylenedioxyphenyl ketone.[1] Oesterle[2] proposed the isomeric structure 2,4,6-trihydroxyphenyl-3,4-methylenedioxystyryl ketone because piperonal was produced by alkaline degradation, along with phloroglucinol and acetopiperone. Butein[3] gave resacetophenone and protocatechuic acid. On the other hand, eriodictyol,[4] homoeriodictyol[5] and hesperitin[6] yielded phloroglucinol and substituted cinnamic acids when subjected to alkaline degradation.

The purpose of the present work was to study the decomposition by alkali of two isomeric chalcones whose structure was known as a result of their synthesis. It was desired to determine the optimum conditions for splitting this type of molecule in order that a procedure might be available for the determination of the structure of naturally occurring chalcones.

The chalcones studied were, 4-hydroxystyryl-phenyl ketone (I) and 4-hydroxyphenyl-styryl ketone (II). These were chosen because the decomposition products could be fairly easily separated and were well-known compounds which could be readily identified.

A series of experiments was carried out in which the chalcones were heated with various concentrations of aqueous potassium hydroxide ranging from 25 to 50% for different periods of time. The net results of a great number of experiments may be summarized as follows.

Aqueous potassium hydroxide caused the splitting of both of these chalcones at the double bond and the decomposition is merely the reverse of their mode of formation, as shown by the equations



$$\underset{\text{I}}{C_6H_5COCH{=}CHC_6H_4(OH)(p)} + H_2O \longrightarrow C_6H_5COCH_3 + C_6H_4\begin{cases}CHO\\OH(p)\end{cases}$$

$$\underset{\text{II}}{C_6H_5CH{=}CHCOC_6H_4OH(p)} + H_2O \longrightarrow C_6H_5CHO + C_6H_5\begin{cases}COCH_3\\OH(p)\end{cases}$$

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[1] Shriner and Kleiderer, THIS JOURNAL, 51, 1267 (1929).

[2] Oesterle, *Schweiz. Apoth.-Ztg.*, 59, 548 (1921).

[3] Auwers and Müller, *Ber.*, 41,4233 (1908).

[4] Will, ibid., 18, 1311 (1885).

[5] Power and Frank, J. *Chem. Soc.*, 91,887 (1907).

[6] Tiemann and Will, *Ber.*, 14, 953 (1881).

It was found that chalcone (II) was decomposed by heating it with 33% potassium hydroxide for six hours. The isomeric chalcone (I) required the use of 50% potassium hydroxide and eight hours of refluxing. The yields of decomposition products were low (25 to 50% of the theoretical) due to secondary reactions of the products with the undecomposed benzalacetophenone derivative to give higher condensation products.[7] It is due to the formation of these products that no actual equilibrium concentrations could be determined for this reversible reaction. Sodium hydroxide cannot be used for these decompositions since the sodium salts of these chalcones are insoluble in the concentrated alkali solutions. In no case was cinnamic acid or *p*-hydroxycinnamic acid found among the decomposition products. The formation of the latter types of degradation products is evidently possible only in the case of highly substituted benzalacetophenones.

Experimental

4-Hydroxystyryl-phenyl Ketone.—Forty grams of acetophenone and 36 g. of *p*-hydroxybenzaldehyde were added to a solution of 24 g. of sodium hydroxide in 200 cc. of water and 100 cc. of alcohol. The mixture was warmed to 70° for two hours and then allowed to stand at room temperature for three days with occasional shaking. The dark red solution was then diluted with an equal volume of water and acidified. The precipitate, which consisted of 4-hydroxystyryl-phenyl ketone and some unreacted *p*-hydroxybenzaldehyde, was filtered, washed with 50% alcohol and then recrystallized twice from 95% alcohol. A yield of 25 g. of yellow needles was obtained which melted at 183–184".

Anal. Subs., 0.2133: CO_2, 0.6235; H_2O, 0.1033. Calcd. for $C_{15}H_{12}O_2$: C, 80.32; H, 5.39. Found: C, 79.91; H, 5.41.

Decomposition of 4-Hydroxystyryl-phenyl Ketone by Alkali.—Ten grams of the above chalcone was refluxed with 200 cc. of 33% aqueous potassium hydroxide for a period of eight hours. The solution became dark red in color and an oil separated on top of the solution. The mixture was cooled and extracted with ether. The ether extract was dried and fractionally distilled. After distillation of the ether the only fraction obtained consisted of 2.5 g. of colorless oil which boiled at 197–202°. This was identified as acetophenone by conversion to the phenylhydrazone,[8] m. p. 105°. The alkaline solution was partly neutralized with hydrochloric acid and evaporated to a volume of about 50 cc. The precipitated potassium chloride was filtered off and the filtrate acidified and filtered again. This filtrate was treated with norite to remove some of the color and then extracted three times with ether. Evaporation of the ether and recrystallization of the residue from a small amount of 50% alcohol gave *p*-hydroxybenzaldehyde, m. p. 116". It was identified by conversion to the phenylhydrazone, which melted at 181–182°. This agrees with the value given by Anselmino.[9]

4-Hydroxyphenyl-styryl Ketone.—Fifty-four grams of *p*-hydroxyacetophenone and 42 g. of benzaldehyde were condensed together by exactly the same procedure as described above for the isomeric chalcone; 57 g. of pale yellow crystals was obtained which melted at 173–174°. This agrees with the value given by Kostanecki and Tambor.[10]

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[7] Kostanecki and Rossbach, *Ber.*, 29, 1488 (1896).

[8] Reisenegger, ibid., 16, 662 (1883).

[9] Anselmino, *ibid.*, 36, 3974 (1903).

[10] Kostanecki and Tambor, *Ber.*, 32, 1924 (1899).

Anal. Subs., 0.2069: CO_2, 0.6068; H_2O, 0.1016. Calcd. for $C_{15}H_{12}O_2$: C, 80.32; H, 5.39. Found: C, 79.99; H, 5.49.

Decomposition of 4-Hydroxyphenyl-styryl Ketone.—Ten grams of this chalcone was refluxed with 200 cc. of 50% aqueous potassium hydroxide for eight hours. Ether extraction of the alkaline solution yielded a small amount of benzaldehyde, b. p. 175–180°, which was identified by means of its phenylhydrazone;[11] m. p. 153–154°. A very small amount of benzyl alcohol was also obtained. This was undoubtedly produced by the Cannizzaro reaction. The alkaline solution produced a brown precipitate on acidification which was dissolved in dilute alkali. The solution was saturated with carbon dioxide which caused the separation of some unreacted chalcone along with some amorphous polymerization products. These were filtered and the filtrate was extracted three times with 100-cc. portions of ether. The ether was distilled and the residue recrystallized from a small amount of water. Crystals of p-hydroxyacetophenone melting at 107° were obtained. It was identified by means of a mixed melting point and conversion to the phenylhydrazone,[12] which melted at 135–136°.

Summary

Concentrated potassium hydroxide splits simple chalcones into the corresponding aldehyde and ketone. The best conditions for accomplishing this degradation and procedures for isolating the products are given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

PREPARATION AND BACTERICIDAL PROPERTIES OF CERTAIN PENTADECANOIC, HEPTADECANOIC AND NONADECANOIC ACIDS. XIX[1]

BY C. M. GREER AND ROGER ADAMS

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In two previous papers covering the preparation and properties of certain dialkyl acetic acids, it was demonstrated that the hexadecanoic acids were more effective bactericidally to B. *Leprae* than the octadecanoic acids, and far more effective than the dodecanoic, the tridecanoic or the tetradecanoic acids. Representatives of the missing series, pentadecanoic, heptadecanoic and nonadecanoic acids have now been prepared. The bacteriological results of the specific compounds produced are given in Table I.

It is obvious that the C_{15} and the C_{17} acids are not as effective as the C_{16}, and the C_{19} acids are less effective than the previously prepared C_{18} acids. From the tables containing the data for all of the acids from C_{12} to C_{19}, it may be concluded that the bactericidal action is zero for the C_{12} acids, and practically nil for the C_{13} acids. Beginning with the C_{14} acids the

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[11] Biltz, Ann., 305, 171 (1899).

[12] Nencki, *Ber.*, 30, 1770 (1897).

[1] The previous paper in this series is XVIII, Armendt and Adams, 52, 1289 (1930).

TABLE I

BACTERIOLOGICAL TESTS TO B. *Leprae*

Dialkyl acetic acids containing C_{15}, C_{17} and C_{19}

	Dilutions of sodium salts in thousands											
	5	25	50	62	74	85	100	125	155	192	250	333
Pentadecanoic **Acids**												
$CH_3CH(CO_2H)C_{12}H_{25}$-*n*	−	−	−	−	+	+	+	+	+	+	+	+
$C_2H_5CH(CO_2H)C_{11}H_{23}$-*n*	−	−	−	−	−	−	±	±	±	+	+	+
$C_3H_7CH(CO_2H)C_{10}H_{21}$-*n*	−	−	−	−	−	±	±	+	+	+	+	+
$C_4H_9CH(CO_2H)C_9H_{19}$-*n*	−	−	−	−	−	±	±	±	+	+	+	+
$C_5H_{11}CH(CO_2H)C_8H_{17}$-*n*	−	−	−	−	−	±	±	+	+	+	+	+
$C_6H_{13}CH(CO_2H)C_7H_{15}$-*n*	−	−	−	−	−	−	+	±	+	+	+	+
Heptadecanoic Acids												
$CH_3CH(CO_2H)C_{14}H_{29}$-*n*	−	−	±	±	±	+	+	+	+	+	+	+
$C_2H_5CH(CO_2H)C_{13}H_{27}$-*n*	−	−	−	−	−	±	+	+	+	+	+	+
$C_3H_7CH(CO_2H)C_{12}H_{25}$-*n*	−	−	−	+	±	+	+	+	+	+	+	+
$C_4H_9CH(CO_2H)C_{11}H_{23}$-*n*	−	−	−	−	±	+	+	+	+	+	+	+
$C_5H_{11}CH(CO_2H)C_{10}H_{21}$-*n*	−	−	−	−	−	±	±	+	+	+	+	+
$C_6H_{13}CH(CO_2H)C_9H_{19}$-*n*	−	−	−	±	+	+	+	+	+	+	+	+
$C_7H_{15}CH(CO_2H)C_8H_{17}$-*n*	−	−	−	−	−	−	−	±	+	+	+	+
Nonadecanoic **Acids**												
$C_3H_7CH(CO_2H)C_{14}H_{29}$-*n*	−	+	+	+	+	+	+	+	+	+	+	+
$C_5H_{11}CH(CO_2H)C_{12}H_{25}$-*n*	−	+	+	+	+	+	+	+	+	+	+	+
$C_7H_{15}CH(CO_2H)C_{10}H_{21}$-*n*	−	+	+	+	+	+	+	+	+	+	+	+

effectiveness reaches a maximum in the C_{16} series, then drops off with a certain irregularity to a very low bactericidal value in the C_{19} acids. Apparently the best combination of physical properties which are presumably causing the bactericidal action, appears in the hexadecanoic compounds. In Table II are given bacteriological results on individual members of the C_{12} to C_{19} acids tested all at one time. The maximum in the hexadecanoic acid is clean cut.

The various acids were prepared in a manner similar to those previously described from the proper disubstituted malonic esters.

TABLE II

BACTERIOLOGICAL TESTS TO B. *Leprae*. SERIES OF DIALKYL ACETIC ACIDS, C_{12}–C_{19}

	No. of *C* atoms	Dilution of sodium salts in thousands					
		5	50	100	155	250	500
$C_7H_{15}CH(CO_2H)CH(CH_3)_2$	12	+	+	+	+	+	+
$C_7H_{15}CH(CO_2H)C_4H_9$	13	−	+	+	+	+	+
$C_7H_{15}CH(CO_2H)C_5H_{11}$	14	−	−	+	+	+	+
$C_7H_{15}CH(CO_2H)C_6H_{13}$	15	−	−	−	−	+	+
$C_7H_{15}CH(CO_2H)C_7H_{15}$	16	−	−	−	−	−	+
$C_7H_{15}CH(CO_2H)C_8H_{17}$	17	−	−	−	+	+	+
$C_7H_{15}CH(CO_2H)C_9H_{19}$	18	−	−	+	+	+	+
$C_7H_{15}CH(CO_2H)C_{10}H_{21}$	19	−	+	+	+	+	+

Experimental Part

TABLE III

CONSTANTS OF ESTERS AND ACIDS

Compound	B. p., °C.	n_D^{20}	d_4^{20}	Found, % C	H
Diethyl dialkyl malonates (all alkyl groups normal)					
$CH_3C(CO_2C_2H_5)_2C_{12}H_{25}$	161–164 (1.5–2.5 mm.)	1.4412	0.9217	70.01	11.1
$C_2H_5C(CO_2C_2H_5)_2C_{11}H_{23}$	150–154 (0.2–1.0 mm.)	1.4420	.9262	70.16	11.25
$C_3H_7C(CO_2C_2H_5)_2C_{10}H_{21}$	143–148 (0.1–1.0 mm.)	1.4416	.9256	70.02	11.12
$C_4H_9C(CO_2C_2H_5)_2C_9H_{19}$	143–147 (0.1–1.0 mm.)	1.4420	.9241	69.95	11.19
$C_5H_{11}C(CO_2C_2H_5)_2C_8H_{17}$	142–146 (0.1–1.0 mm.)			70.28	11.17
$C_6H_{13}C(CO_2C_2H_5)_2C_7H_{15}$	146–152 (0.1–1.0 mm.)	1.4412	.9231	70.14	11.18
Calcd. for each isomer of $C_{20}H_{38}O_4$				70.11	11.19
Pentadecanoic Acids					
$CH_3CH(CO_2H)C_{12}H_{25}$	172–175 (2–3 mm.) m. p. 34–36			74.66	12.58
$C_2H_5CH(CO_2H)C_{11}H_{23}$	160–163 (2–3 mm.)	1.4455	0.8821	74.24	12.42
$C_3H_7CH(CO_2H)C_{10}H_{21}$	164–167 (2–3 mm.)	1.4450	.8819	74.32	12.51
$C_4H_9CH(CO_2H)C_9H_{19}$	159–162 (2–3 mm.)	1.4459	.8824	74.20	12.46
$C_5H_{11}CH(CO_2H)C_8H_{17}$	161–164 (2–3 mm.)			74.20	12.37
$C_6H_{13}CH(CO_2H)C_7H_{15}$	156–159 (1–2 mm.)	1.4450	.8806	74.38	12.55
Calcd. for each isomer of $C_{15}H_{30}O_2$				74.31	12.48

TABLE IV

CONSTANTS OF ESTERS AND ACIDS

Compound	B. p., °C.	n_D^{20}	d_4^{20}	Found, % C	H
Diethyl dialkyl malotiates (all alkyl groups normal)					
$CH_3C(CO_2C_2H_5)_2C_{14}H_{29}$	172–176 (0.5–1.0 mm.)	1.4436	0.9164	71.20	11.53
$C_2H_5C(CO_2C_2H_5)_2C_{13}H_{27}$	178–181 (0.8–2.0 mm.)	1.4435	.9207	70.95	11.33
$C_3H_7C(CO_2C_2H_5)_2C_{12}H_{25}$	173–177 (0.5–1.0 mm.)	1.4438	.9191	71.33	11.40
$C_4H_9C(CO_2C_2H_5)_2C_{11}H_{23}$	171–176 (0.5–1.0 mm.)	1.4439	.9173	71.21	11.42
$C_5H_{11}C(CO_2C_2H_5)_2C_{10}H_{21}$	148–154 (0.1–0.8 mm.)			71.31	11.35
$C_6H_{13}C(CO_2C_2H_5)_2C_9H_{19}$	170–174 (0.5–1.5 mm.)	1.4441	.9178	71.20	11.39
$C_7H_{15}C(CO_2C_2H_5)_2C_8H_{17}$	157–161 (0.2–1.0 mm.)	1.4436	.9171	71.40	11.36
Calcd. for each isomer of $C_{22}H_{42}O_4$				71.29	11.43
Heptadecanoic Acids					
$CH_3CH(CO_2H)C_{14}H_{29}$	174–177 (1–2 mm.) m. p. 45.5–47.5[a]			75.77	12.67
$C_2H_5CH(CO_2H)C_{13}H_{27}$	164–168 (1–2 mm.)	1.4480	0.8810	75.27	12.68
$C_3H_7CH(CO_2H)C_{12}H_{25}$	183–187 (2.5–3.5 mm.)	1.4483	.8827	75.63	12.72
$C_4H_9CH(CO_2H)C_{11}H_{23}$	174–177 (2–3 mm.)	1.4484	.8783	75.35	12.61
$C_5H_{11}CH(CO_2H)C_{10}H_{21}$	177–182 (2–3 mm.)			75.94	12.50
$C_6H_{13}CH(CO_2H)C_9H_{19}$	182–185 (2–3 mm.)	1.4489	.8821	75.31	12.59
$C_7H_{15}CH(CO_2H)C_8H_{17}$	184–187 (2–3 mm.)	1.4483	.8780	75.44	12.71
Calcd. for each isomer of $C_{17}H_{34}O_2$				75.48	12.68

[a] M. p. 54° according to Morgan and Holmes, *J. Soc. Chem.* Ind., 46, 152 (1927).

TABLE V

CONSTANTS OF ESTERS AND ACIDS

Compound	B. p., °C.	n_D^{20}	d_4^{20}	Found, % C	H
Diethyl dialkyl malonates (all alkyl groups normal)					
$C_3H_7C(CO_2C_2H_5)_2C_{14}H_{29}$	180–184 (0.2–1.0 mm.)	1.4459	0.9141	72.29	11.63
$C_5H_{11}C(CO_2C_2H_5)_2C_{12}H_{25}$	178–181 (0.2–1.0 mm.)	1.4460	.9112	72.30	11.58
$C_7H_{15}C(CO_2C_2H_5)_2C_{10}H_{21}$	182–186 (0.2–1.0 mm.)	1 4459	.9116	72.23	11.71
Calcd. for each isomer of $C_{24}H_{46}O_4$				72 29	11.64
Nonadecanoic Acids					
$C_3H_7CH(CO_2H)C_{14}H_{29}$	182–185 (0.5–1.5 mm.)	m. p. 35–37		76.56	12.81
$C_5H_{11}CH(CO_2H)C_{12}H_{25}$	184–188 (0.5–1.5 mm.)	1.4508	0.8752	76.47	12.85
$C_7H_{15}CH(CO_2H)C_{10}H_{21}$	180–184 (0.5–1.5 mm.)	m. p. 31.5–33.5		76.65	12.81
Calcd. for each isomer of $C_{19}H_{38}O_2$				76.43	12.84

Summary

A number of pentadecanoic, heptadecanoic and nonadecanoic acids have been prepared and tested bacteriologically toward B. Leprae. The C_{15} and the C_{17} acids are active but not to such a degree as the previously studied hexadecanoic acids. The C_{19} acids are very slightly bactericidal.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE REDUCTION OF NICOTINE AND SOME DERIVATIVES OF HEXA- AND OCTAHYDRONICOTINES

BY WALLACE WINDUS AND C. S. MARVEL

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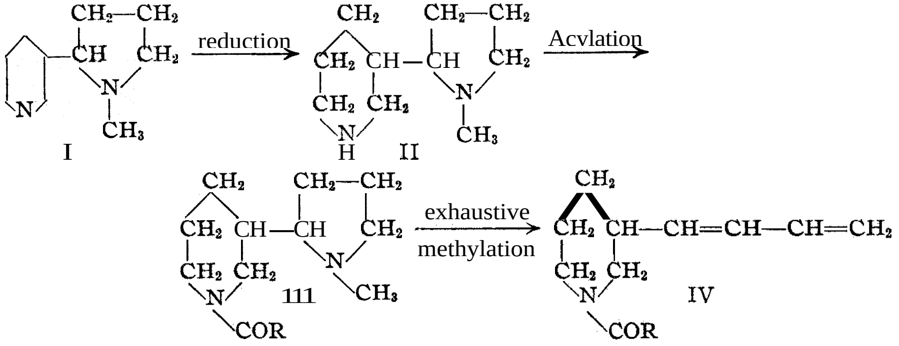
Nicotine (I) should be the cheapest basic product for the preparation of a piperidine ring with an unsaturated side chain in the beta position (IV), provided the following reactions proceed in the normal manner.



The reduction of nicotine by means of sodium and alcohol was first studied by Liebrecht,[1] who isolated a basic product which he called di-

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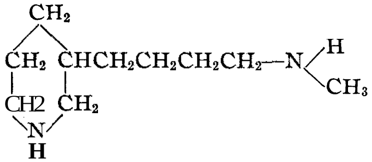
[1] Liebrecht, *Ber.*, 18, 2969 (1885); 19, 2587 (1886).

piperidyl. He prepared and analyzed a number of derivatives. A few years later Blau[2] made a more complete investigation of the reaction and showed that Liebrecht's base was not dipiperidyl, but was a mixture of two amines which he called hexahydronicotine (II) and octahydronicotine. The second compound is formed by the opening of the pyrrolidine ring in the reduction and presumably has the formula



Blau did not establish the relative amounts of these reduction products, but he did isolate both amines and prepare a number of derivatives. Pinner[3] has also studied the reduction of nicotine with sodium and alcohol and has reported the isolation of hexahydronicotine only.

In attempting to carry out the synthesis outlined above, nicotine has been reduced with sodium and alcohol and its hydrochloride has been reduced with hydrogen under pressure using the platinum-oxide platinum black catalyst of Adams and Shriner.[4] The relative amounts of hexahydronicotine and octahydronicotine obtained in these reductions were determined by benzoylating the mixed amines and separating the monobenzoyl derivative of the former from the dibenzoyl derivative of the latter by fractional distillation under reduced pressure. It was found that the sodium and alcohol reduction of nicotine produced approximately five parts of hexahydronicotine to one part of octahydronicotine. On the other hand, catalytic reduction of the hydrochloride produced about one part of hexahydronicotine to three parts of octahydronicotine.

The acetyl and benzoyl hexahydronicotines (III) were treated with methyl iodide and the quaternary ammonium iodides were easily obtained. However, distillation of the corresponding hydroxides gave unexpected results. The acetyl derivative lost methyl alcohol to give back the original acyl derivative of hexahydronicotine almost quantitatively. The benzoyl derivative gave very complex mixtures and the only product definitely identified was the original acyl derivative. Since neither reaction seemed to offer any promise as a method of obtaining the desired unsaturated piperidines, further work was discontinued.

It is interesting to note that reduction gave optically active hexahydronicotine derivatives, but optically inactive octahydronicotine derivatives.

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[2] Blau, *Ber.*, 24, 326 (1891); **26,** 628, 1029 (1893).

[3] Pinner, *ibid.*, **26,** 765 (1893).

[4] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

Experimental Part

Reduction of Nicotine **with** Sodium and Alcohol.—The procedure was essentially that used by Liebrecht,[1] Blau[2] and Pinner.[3] In one typical reduction the amounts used were 150 g. of nicotine, 2000 cc. of absolute alcohol and 130 g. of sodium. About 500 cc. of water was added. The alcohol was distilled and the residue was extracted with ether. Two such runs were combined and after distillation of the ether the residue was distilled under reduced pressure. There was thus obtained 98 g. of mixed bases boiling at 125–140" at 16 mm.; d_4^{20} 0.9800; n_D^{20} 1.5067.

Benzoylation of the Mixed Amines.—In a 500-cc. glass-stoppered bottle were placed 50 g. of the mixed amines and 120 g. of 10% aqueous sodium hydroxide solution. The mixture was cooled in an ice-bath and 50 g. of benzoyl chloride was added slowly with shaking. The shaking was continued until the odor of benzoyl chloride was no longer apparent. The mixed amides were then extracted with ether and the ether solution was dried and distilled. The amides were separated by fractional distillation under reduced pressure. There were thus obtained 48 g. of monobenzoylhexahydronicotine boiling at 195–198° at 0.8–1.0 mm.; d_4^{20} 1.072; n_D^{20} 1.5549; $[\alpha]_D^{20}$ $-11.39°$ (0.1903 g. in 25 cc. of absolute alcohol), and 8 g. of dibenzoyloctahydronicotine boiling at 280–300° at 1.5 mm.; d_4^{20} 1.106; n_D^{20} 1.5710. The dibenzoyl derivative was never obtained quite pure, as was shown by the wide boiling range and the nitrogen analysis. It was optically inactive.

Anal. (Dumas) Calcd. for $C_{17}H_{24}ON_2$: N, 10.29. Found: N, 10.38; 10.44. Calcd. for $C_{24}H_{30}O_2N_2$: N, 7.40. Found: N, 7.15.

Catalytic Reduction of Nicotine Hydrochloride.—Pure nicotine hydrochloride was prepared by dissolving 100 g. of nicotine in 400 cc. of dry ether and then passing in dry hydrogen chloride. The salt which precipitated was filtered off and recrystallized by dissolving in the minimum amount of hot absolute alcohol, adding anhydrous ether and cooling. This procedure gave 116 g. (80% of the theoretical amount) of nicotine hydrochloride melting at 163–165".

The hydrochloride was reduced according to the general method of reducing pyridine derivatives recently described by Hamilton and Adams.[5] The individual runs were made with 0.2 of a mole of nicotine hydrochloride using 0.4 g. of catalyst. The reduction was run at 70°. The absorption of hydrogen seemed to be complete in about six hours. Altogether 160 g. of salt was reduced. After the reduction the solutions were combined, filtered and concentrated. The residue was treated with aqueous potassium hydroxide, the amine layer was extracted with ether and then dried over solid potassium hydroxide. On distillation there was obtained 86 g. of mixed bases boiling at 128–130° at 16 mm.; n_D^{20} 1.4858; d_4^{20} 0.9192.

The chloroplatinate of this material melted at 199–200°, which agrees with the m. p. recorded by Blau[2] for this derivative of octahydronicotine. Benzoylation of 50 g. of this base was carried out as described before. Fractionation of the mixed amides gave 11.5 g. of monobenzoylhexahydronicotine, b. p. 208–212° at 2 mm., and 39.5 g. of dibenzoyloctahydronicotine, b. p. 300–305" at 2 mm.

Acetylhexahydronicotine.—To 50 g. of a mixture of the bases from the sodium and alcohol reduction of nicotine was slowly added 30 g. of acetic anhydride. The mixture was kept cold and shaken while the two substances were reacting. The mixture was then distilled. Several portions were obtained. The two main fractions were collected at 140–150° (1 mm.) and 210–213° (1 mm.). These were analyzed and agreed with acetylhexahydronicotine and diacetyloctahydronicotine, respectively.

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[5] Hamilton and Adams, THIS JOURNAL, 50, 2260 (1928).

Acetylhexahydronicotine had the following constants: d_4^{20} **1.034;** n_D^{20} **1.5010**; calcd. M_D **61.16;** found, M_D **60.16;** $[\alpha]_D^{20}$, **−4.07°** **(0.2130** g. in **25** cc. of absolute alcohol).

Anal. (Dumas) Calcd. for $C_{12}H_{22}N_2O$: N, **13.32.** Found: N, **13.51.**

Diacetyloctahydronicotine had the following constants: d_4^{20} **1.041;** n_D^{20} **1.5033;** calcd. M_D, **72.32;** found, M_D, **72.21.** It was optically inactive.

Anal. (Dumas) Calcd. for $C_{14}H_{26}N_2O_2$: N, **11.01.** Found: **N, 10.96.**

Methiodide of **Benzoylhexahydronicotine.**—To a solution of **113** g. of benzoylhexahydronicotine in **250** cc. of dry ether was added **65** g. of methyl iodide. Crystals began to form in a very short time. After twelve hours the precipitate was filtered and washed with dry ether. The salt was hygroscopic and was dried over phosphorus pentoxide in a vacuum desiccator. There was thus obtained **144** g. of salt which softened at about 85° and melted at **99–103°** with decomposition.

Anal. (Volhard) Calcd. for $C_{18}H_{27}N_2OI$: **I, 30.64.** Found: I, **30.42, 30.56.**

Methiodide of **Acetylhexahydronicotine.**—To **20** g. of acetylhexahydronicotine in dry ether was added an excess of methyl iodide. The derivative separated as an oily product which would not crystallize.

Distillation of Quaternary Ammonium Hydroxide from the Methiodide of Acetyl **Hexahydronicotine.**—Some of the oily methiodide was dissolved in water and the iodine content of this solution was determined. It was thus found that 14.3 g. of the methiodide was in solution. This solution was treated with an excess of silver oxide and shaken until the aqueous portion no longer gave a test for the iodide ion. The mixture was then filtered, the precipitate was washed with water several times and the filtrate and washings were evaporated, first under ordinary pressure and finally under reduced pressure until the water was removed. The residue was then heated and finally distilled at **1.1** mm. This gave **7** g. of product boiling at 142–148° at **1.1 mm.;** d_4^{20} **1.017;** n_D^{20} **1.4984.** This material was very pure acetylhexahydronicotine.

Anal. (Dumas) Calcd. for $C_{12}H_{22}N_2O$: N, **13.32.** Found: **N, 13.55, 13.58.**

Distillation of **the** Quaternary Ammonium Hydroxide from the Methiodide of **Benzoylhexahydronicotine.**—A solution of **154** g. of the methiodide in **300** cc. of water was treated with **41 g.** of silver oxide. The mixture was treated as described for the corresponding acetyl derivative. Fractionation of the decomposition products gave several different substances. The main fraction boiled at 140–147° at **1.2** mm. Analysis of this material showed that it was not the expected exhaustive methylation product. A small portion **(5** g.) boiling at 192–200° **(1.2** mm) was found to be benzoylhexahydronicotine.

Summary

1. Reduction of nicotine with sodium and alcohol produced a mixture of amines which contained about five parts of hexahydronicotine for one part of octahydronicotine.

2. Catalytic reduction of nicotine hydrochloride with hydrogen and a platinum–oxide platinum black catalyst gave a mixture of amines which contained about one part of hexahydronicotine to three parts of octahydronicotine.

3. Attempts to obtain piperidine derivatives with unsaturated side chains in the β-position by the exhaustive methylation of benzoyl and acetyl hexahydronicotines were unsuccessful.

URBANA, ILLINOIS

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE OXIDATION OF "DI-ISOBUTYLENE" BY OZONE

BY ROBERT J. MCCUBBIN AND HOMER ADKINS

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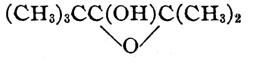
An octylene or a mixture of octylenes known as di-isobutylene was obtained by Butlerow[1] on heating equal weights of tertiary butyl alcohol, water and sulfuric acid in a water bath for twenty-four hours. Butlerow oxidized di-isobutylene with potassium dichromate and obtained carbon dioxide, acetone, acetic acid, trimethylacetic acid, a seven-carbon atom ketone (b. p. about 124°) and an eight-carbon atom acid (b. p. 205–218°). When he used a 5% solution of potassium permanganate as an oxidizing agent he obtained the three acids but neither of the ketones mentioned above. There was also produced a monohydroxy alcohol (m. p. 49–50°) to which he assigned the name of oxoctenol and the formula I and an hydroxy acid (m. p. 117°) to which he assigned the name oxoctylic acid and the formula II.

(I) 

$(CH_3)_3C\underbrace{C(OH)C}_{O}(CH_3)_2$

Epoxy-2,3-trimethyl-2,4,4-pentanol-3

(II) $(CH_3)_3CCH_2C(OH)(CH_3)COOH$

Trimethyl-2,4,4-hydroxy-2-pentane acid-1

Prileshaiev[2] oxidized di-isobutylene with a 1% solution of magnesium permanganate and obtained almost equal quantities of oxoctenol and a glycol (formula III) and small amounts of acetone, trimethylacetic acid and oxoctylic acid. When he used a 1% solution of potassium permanganate the amount of the glycol was three and a half times the amount of oxoctenol.

(III) $(CH_3)_3CCH_2C(OH)(CH_3)CH_2OH$
Trimethyl-2,4,4-pentanediol-1,2

(IV) $(CH_3)_3CCH{=}C(CH_3)_2$
Trimethyl-2,4,4-pentene-2,3

(V) $(CH_3)_3CCH_2C(CH_3){=}CH_2$
Trimethyl-2,4,4-pentene-1,2

The above facts substantiate the view of Butlerow that di-isobutylene contains two isomers having the formulas IV and V. The present investigation was carried on for the purpose of evaluating the proportions of the isomers in the mixture and of developing practical methods for the production of such ketones, aldehydes and acids as could be obtained in good quantities from the readily available di-isobutylene. The di-isobutylene used in this investigation was prepared as by Edgar.[3] The material used had a boiling range of 101–103°. A similar product was obtained through the polymerization of isobutylene in 65% sulfuric acid, the isobutylene having been prepared by dehydrating isobutyl alcohol over alumina at 400°

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[1] Butlerow, *Ann.*, **189**, 46–83 (1877).

[2] Prileshaiev, *J. Russ. Phys.-Chem. Soc.*, **39**, 769–771 (1907).

[3] Edgar, *Ind. Eng. Chem.*, **19**, 746 (1927).

This method of polymerization gave only low yields of di-isobutylene, as the principal product was tri-isobutylene.[4]

Preparation of Ozone.—Oxygen from a commercial cylinder was passed at the rate 15 liters per hour through an ozonizer consisting of three Berthelot tubes arranged essentially as described by Lee I. Smith[5] except that the inner mercury electrode was replaced by a 20% solution of sulfuric acid. The oxygen was dried over sulfuric acid and phosphorus pentoxide before passing through the ozonizer. The gas from the ozonizer contained from 3 to 4% of ozone. The ozonization was carried out in a series of three 300-ml. long-necked flasks provided with ground-glass joints. The solution of di-isobutylene was placed in the first two of the reaction flasks while the third was used as a trap. The exit gases from the third flask passed through a sulfuric acid wash bottle.

The Formation and Hydrolysis of the Ozonide of Di-isobutylene.—Preliminary experiments in which the ozonization was carried on in a chloroform solution were unsuccessful, as difficulty was encountered in decomposing the ozonide without using zinc. Acetic acid was thereafter used as a solvent. Fifty-six g. of di-isobutylene, dissolved in 100 ml. of acetic acid containing about 1% of acetic anhydride, was placed in each of the two reaction flasks and ozone passed into the flask for about twenty-four hours, at the end of which time the ozone passed through unchanged in concentration. The yield of ozonide was then determined by titrating a weighed sample of its acetic acid solution, the ozonide $C_8H_{16}O_3$ being assumed to constitute the whole of the non-acidic portion of the solution. The yield of ozonide was about 50% of the theoretical.

An amount of water approximately equal to the weight of acetic acid present (as determined by the above titration) was added to the ozonide solution. The mixture was placed in a 2-liter, three-necked flask in which was fitted a mechanical stirrer and a long reflux condenser. The amount and temperature of the water in the condenser were regulated to control the amount of refluxing. This condenser was connected at the upper end to a well-cooled condenser by means of a piece of 1-cm. glass tubing. The condensate was collected in a flask cooled in ice water. About 20 g. of zinc (30-mesh) was added to the solution in 2- or 3-gram portions over a period of one and one-half to two hours. The reaction proceeded with the evolution of a good deal of heat and it was necessary to cool the reaction flask with ice water. The mixture was stirred rapidly so that there was practically an emulsion of the ozonide and its decomposition products in the dilute acid. When the reaction had moderated somewhat (about one and one-half hours), the cooling bath was removed from around the flask and it was warmed with a small free flame.

When most of the zinc had gone into solution, the flask was heated sufficiently to cause gentle refluxing. By keeping the temperature of the water in the reflux condenser at about 70° the more volatile aldehydes and ketones distilled over with water and were accompanied by only a relatively small amount of acetic acid. The heating and stirring were continued until no more insoluble oil distilled, water being added to the distilling flask in such amounts that the volume remained nearly constant. The oily layer of the distillate was separated and dried over calcium chloride. The aqueous layer was dis-

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[4] Mr. Walter Arthur, at the suggestion of Dr. James F. Norris, began in the fall of 1926 at the Massachusetts Institute of Technology an investigation of the oxidation of di-isobutylene. Simultaneously and independently the authors began a similar study. A year later Mr. Arthur came to Wisconsin to continue his graduate work and the duplication of work was discovered. Mr. Arthur with the approval of Dr. Norris continued his study of the permanganate oxidation of di-isobutylene and expects to report on this independently.

[5] Lee I. Smith, THIS JOURNAL, 47, 1844 (1925).

tilled several times over calcium chloride and the oily layer obtained in this way was added to the first portion. The oil was dried over calcium chloride and fractionated through a 20-em. Widmer column. The results from a typical fractionation are shown in Table I. They were duplicated in six experiments.

TABLE I

FRACTIONATION OF THE HYDROLYSIS PRODUCTS OF THE OZONIDE OF DI-ISOBUTYLENE

Fraction	Boiling range	Weight, g.	Fraction	Boiling range	Weight, g.
A	to 65°	4.8	E	100–110	1.1
B	65– 77	7.7	F	110–120	14.4
C	77– 90	0 8	G	120–130	38.1
D	90–100	0.2	H	Residue	10.3

The fraction boiling up to 65° was identified as acetone by means of the dibenzal derivative, m. p. 111°; and as the *p*-nitrophenylhydrazone, m. p. 148°. Fraction B formed a semicarbazone melting at 190.7' (corr.), which corresponds with the melting point of trimethylacetaldehyde semicarbazone (191°). This fraction was also oxidized to an acid boiling at 162–165° which formed an amide melting at 153" (corr.). Trimethylaceticacid boils at 163.7° and its amide melts at 153–154°. The fractions boiling between 100 and 130° were washed with water and-sodium carbonate solution for the removal of acetic and formic acids. The resulting oil after drying over calcium chloride or sodium sulfate weighed 40 g., distilled between 123–126" and gave a semicarbazone melting at 176' (corr.).

Anal. Calcd. for $C_7H_{14}O$: C, 73.62; H, 12.36. Found: C, 73.33; H, 12.51.

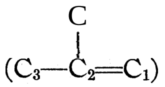
Anal. Calcd. for $C_8H_{17}N_3O$: N, 24.54. Found: N, 24.65.

Markownikoff[6] claimed that the semicarbazone of ethyl tertiary butyl ketone melted at 174–175°. Favorski[7] reported that the melting point of this semicarbazone was 144°. Ethyl tertiary butyl ketone was synthesized and the melting point of its semicarbazone found to be 144°. An attempt to synthesize the isomeric neopentyl methyl ketone from acetoacetic ester and tertiary butyl bromide resulted in a failure.

The ketone boiling at 123–126° upon oxidation with dichromate was converted into two acids, one of them boiling mainly at 164–165" and the other at 175–180°. The acids formed amides melting at 153.5 and 126°, respectively. The amide of trimethylacetic acid melts at 153–154° and that of tertiary butyl acetic acid at 132°. All of the above facts point to a ketone having the structure $(CH_3)_3CCH_2COCH_3$, *i.e.*, methyl neopentyl ketone or dimethyl-4,4-pentanone-2.

In addition to the products referred to above, *i.e.*, acetone, trimethylacetaldehyde and methyl neopentyl ketone, there were also formed during the hydrolysis of the ozonide considerable quantities of formaldehyde and carbon dioxide.

Acetone and trimethylacetaldehyde were formed in approximately equal amounts (0.082 and 0.089 moles, respectively) and are presumably oxidation products of an octene of formula IV. The amount of methyl neopentyl ketone produced was approximately 3.7 times the amounts of acetone and trimethylacetaldehyde and indicates a corresponding predominance of an octene of formula V. This is in good agreement with Prileshaiev's conclusions as to the ratio of the isomers as determined by oxidation of the mixture of isomers using a 1% solution of potassium permanganate.

Isobutylene  $(C_3\text{—}\overset{\overset{\displaystyle C}{|}}{C_2}\text{=}C_1)$ may add to isobutylene in at least four ways.

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[6] Markownikoff, ***Ber.*, 33,** 1906 (1900).

[7] Favorski, J. *Russ. Phys.-Chem. Soc.*, *44*, 1339–1395 (1912).

(1) The hydrogen of the methylene group of one molecule may add: (a) to the number 1 carbon atom or (b) to the 2 carbon of the second molecule. *(2)* The hydrogen of one of the methyl groups in the first molecule may add (a) to the number 1 carbon atom or (b) to the number 2 carbon atom of the second molecule. The predominance of the octene of formula V indicates that in the polymerization of isobutylene the reaction proceeds predominantly according to 2a, *i.* e., the labile hydrogen for addition is in the methyl rather than in the methylene group, and the preferred direction of addition involves the addition of hydrogen to the more hydrogenated carbon atom. It should be noted that the presence of an octene of formula IV in the mixture does not necessarily indicate that addition took place according to scheme 1a since sulfuric acid would be expected to cause the rearrangement of an octene of formula V to one of formula IV.

Summary

Methyl neopentyl ketone, $(CH_3)_3CCH_2COCH_3$, and trimethylacetaldehyde were produced in the ratio of approximately **3.7** to 1 when di-isobutylene was ozonized and the ozonide hydrolyzed. This indicates that di-isobutylene contains two isomeric octylenes, **i.** e., trimethyl-2,4,4-pentene-1,2 and trimethyl-2,4,4-pentene-2,3, with the former in considerable excess. It appears then that when isobutylene undergoes polymerization the labile hydrogen for addition is in the methyl rather than in the methylene group, and that the predominant direction of additions involves the addition of hydrogen to the more hydrogenated carbon atom.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

NITROFURFURAL AND NITROFURYLACRYLIC ACID

BY HENRY GILMAN AND GEORGE F. WRIGHT

RECEIVED MARCH 17, 1930 PUBLISHED JUNE 6, 1930

Introduction

In connection with the preparation of aminofurans and their diazo compounds, it was necessary to have a series of readily accessible nitrofurans and their derivatives. We turned to the nitration of furfural because this aldehyde is available in large quantities and at a low price. Apparently, the literature contains no description of the preparation of a nitrofurfural. However, attempts have been made to nitrate furfural.[1]

By means of the technique of Gilman and Wright[2] for introducing substituents in furfural, we have succeeded in preparing the first nitrofurfural. As might have been predicted, the nitro group markedly increases

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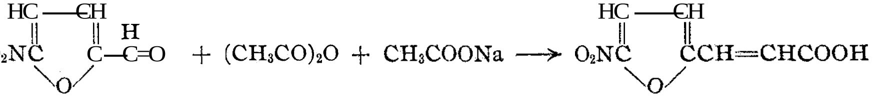
[1] **Marquis,** *Compt.* **rend., 135,** 505 (1902).

[2] Gilman **and Wright,** THIS JOURNAL, **52,** 1170 (1930).

the stability of the furan nucleus.[2] The nitrofurfural has been characterized by a few selected derivatives. Among the reactions studied was a Perkin condensation leading to nitrofurylacrylic acid. The same nitrofurylacrylic acid was obtained by the nitration of furylacrylic acid and of its ethyl ester. However, the mechanism of the nitration of furfural diacetate is apparently unlike that of furylacrylic acid. In the latter case, it is unnecessary to close the furan ring with pyridine (see Experimental Part) inasmuch as the nitrofurylacrylic acid is precipitated directly in the nitrating mixture.[3]

The nitrofurfural was oxidized to the known nitrofuroic acid of Klinkhardt[4] and of Marquis.[5] If we provisionally accept the structure of nitrofuroic acid assigned by Hill and Palmer,[5] then our nitro group is in the 5-position,[6] and the following reaction illustrates the condensation leading to the 5-nitrofurylacrylic acid.



Experimental Part

Nitrofurfural Diacetate, $NO_2C_4H_2OCH(OCOCH_3)_2$.—The nitrating mixture was prepared by adding dropwise 43.7 g. (0.69 mole) of fuming nitric acid (sp. gr. 1.5) to 143 g. (1.4 moles) of acetic anhydride chilled to 0° and contained in a 500-cc. three-necked flask equipped with a mechanical stirrer, dropping funnel and thermometer. A solution of 49.5 g. (0.25 mole) of furfural diacetate[7] in 51 g. (0.5 mole) of acetic anhydride was added slowly to the nitrating mixture which was not allowed to rise above $-5°$. The time required for the addition was about thirty minutes. After allowing the reaction mixture to stir for three hours longer, it was poured into about one kilo of cracked ice. A sodium hydroxide solution (about 40%) was then added, with *vigorous* stirring, until precipitation of the oil was complete. The aqueous layer was then removed by decantation, and an almost equal volume of pyridine[8] was added very carefully and slowly, together with some cracked ice. Care must be exercised that the reaction starts after a few cc. of pyridine are added; otherwise the entire reaction mixture may be lost by violent ebullition. The mixture is diluted to 2 or 3 times its original volume by

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[3] A later paper will consider 1,4- and 1,6-addition reactions of furan types as a mechanism of nuclear substitution; see Gilman, Kirby and Kinney, THIS JOURNAL, 51, 2252 (1929).

[4] Klinkhardt, *J. prakt. Chem.*, *25*, 41 (1882).

[5] Marquis, *Ann. chim. phys.*, [8] 4, 196 (1905). See also Priebs, *Ber.*, 18, 1363 (1885), and Hill and Palmer, *Am. Chem. J.*, *10*, *380* (1888).

[6] Marquis (Ref. 5) has assigned the nitro group in his nitrofuroic acid to either the 3- or the 4-position. We hope definitely to establish the position of the nitro group by a series of moderate and reliable reactions. In our bromination of furfural diacetate (Ref. 2), the bromine entered the 5-position.

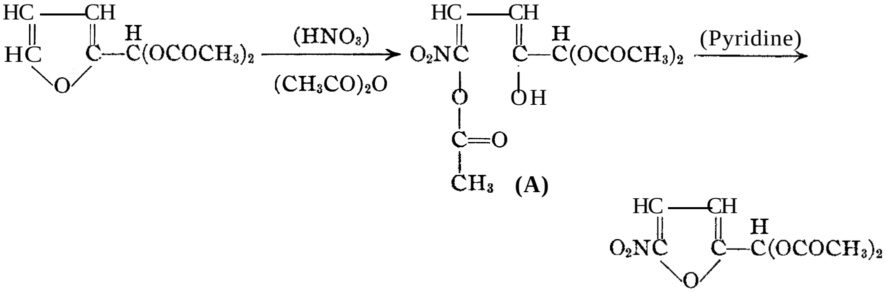
[7] The furfural diacetate was prepared in accordance with the directions of Gilman and Wright, *Iowa State College J. of Science*, 4, 35 (1929). The yields reported in that article are rather modest. It has since been determined that the yields are in the range of 70%.

[8] The excess of pyridine appears to be essential.

means of iced water, and after standing until precipitation is complete (about one-half hour), the cold solution is filtered by suction, and washed free of pyridine by dilute acetic acid followed by a water washing. The crude nitrofurfural diacetate obtained in this manner weighs, when air-dried, 24.5 g. or 40% of the theoretical amount, and melts at 87°. It may be crystallized from hot alcohol and when purified it melts at 92.5°.

Anal. Calcd. for $C_9H_9O_7N$: C, 44.44; H, 3.73. Found: C, 44.85; H, 3.81.

Intermediate **Ring** Fission Compound.—It is possible to isolate the intermediate nitro compound prior to its closure by pyridine. If we assign to this intermediate a structure that conforms with that ascribed by Marquis[5] to the fission products of nitrofuran and nitrofuroic acid, the reaction with pyridine may be written



The heavy oil [Compound (A)] precipitated by addition of cracked ice to the reaction mixture, is extracted with ether, and after washing the ether solution with water and then chilling it, pyridine is added to neutralize the acids present.[9] The ether solution is then washed thoroughly with water, dried over sodium sulfate, filtered, and then concentrated by evaporation under reduced pressure until crystallization is complete. The product obtained by suction filtration weighs 31.6 g. (42% yield), melts 96–97", and, when crystallized from a petroleum ether–benzene mixture, melts at 106–107°.

Anal. Calcd. for $C_{11}H_{13}O_9N$: C, 43.56; H, 4.32. Found: C, 43.03; H, 4.53.

When the intermediate compound (A) is dissolved in pyridine and then precipitated by dilution with water, it is converted quantitatively to the nitrofurfural diacetate melting at 92–93'. Inasmuch as this reaction is slightly endothermic, it is evidently necessary to maintain sufficient heat in the treatment of the precipitated oil in the original preparation of nitrofurfural diacetate to allow this ring closure by pyridine to take place.

Nitrofurfural, $NO_2C_4H_2OCHO$.—In an atmosphere of carbon dioxide, 24.3 g. (0.1 mole) of nitrofurfural diacetate was refluxed, with constant stirring, with a solution of 54 g. of concd. sulfuric acid in 108 g. of water for about fifteen minutes. The ether extract of the cooled hydrolysate was washed with water, dried over sodium sulfate, and then (after removing the ether) distilled at 128–132° (10 mm.). The yield was 10.95 g., or 77.8%. The nitrofurfural melted at 35–36° after crystallization from petroleum ether. It is colorless when pure and is somewhat soluble in water.

Anal. Calcd. for $C_5H_3O_4N$: C, 42.55; H, 2.14. Found: C, 42.64; H, 2.18.

Oxidation of 1.41 g. (0.01 mole) of the nitrofurfural by an equivalent quantity of sodium dichromate in sulfuric acid gave 0.64 g. or a 57% yield of crude nitrofuroic acid. This melted at 183° when crystallized from water and showed no depression in a mixed melting point determination with the acid prepared in accordance with the directions of

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[9] The point of neutralization may be determined by means of litmus paper and by noting the cessation of temperature rise during addition of the pyridine.

Marquis.[5] Marquis had previously shown that his nitrofuroic acid was identical with that of earlier investigators.[4,5]

It is interesting to note that the same nitrofuroic acid was obtained by us by oxidizing nitrofurfural diacetate with aqua regia.

Nitrofurfuraldoxime, $NO_2C_4H_2OCH{=}NOH$.—The oxime was prepared in a customary manner from hydroxylamine hydrochloride (10.4 g. or 0.15 mole), sodium hydroxide and 17.7 g. (0.073 mole) of nitrofurfural diacetate. Because of the sensitivity of the nitro group to alkali, the 6 g. (0.15 mole) of sodium hydroxide was added slowly, as a dilute solution, and with vigorous shaking. The yield of oxime melting at 121° was 8.0 g. or 70%. It is slightly sweet.[10]

The isomeric oxime is more readily prepared from nitrofurfural by a similar reaction. When crystallized from alcohol it melts at 153°. If the hydrochloride of the oxime melting at 121° is precipitated by sodium carbonate, it yields the higher-melting (153°) isomer.

Anal. Calcd. for $C_5H_4O_4N_2$: C, 38.46; H, 2.58. Found: C, 38.84; H, 2.72.

Nitrofurylacrylic Acid, $NO_2C_4H_2OCH{=}CHCO_2H$.—A mixture consisting of 14.1 g. (0.058 mole) of nitrofurfural diacetate, 40 g. (0.4 mole) of acetic anhydride, 20.0 g. (0.24 mole) of thrice fused sodium acetate[n] and a drop of pyridine was refluxed at 142" for eight hours with constant stirring. The reaction mixture was diluted with about 300 cc. of water, and sodium carbonate was added to neutrality. It was then heated to 90° with boneblack, filtered and acidified; the nitrofurylacrylic acid which separated melted at 229–230° and weighed 1.2 g. or 13% of the theoretical.[12] When crystallized from methyl alcohol, or preferably from furfural, it melted at 235–236°. It is of interest to observe that in this reaction the nitro-aldehyde diacetate and not the free aldehyde was used in the condensation. This points to the intermediate formation of a diacetate in the Perkin reaction.

In an experiment carried out under corresponding conditions, but starting with nitrofurfural (0.04 mole), the yield of nitrofurylacrylic acid was 27.4%.

The nitrofurylacrylic acid appears to be distinctly more stable than the corresponding unsubstituted furylacrylic acid. For example, it was apparently unaffected by chromic acid, which will oxidize furylacrylic acid.

Anal. Calcd. for $C_7H_5O_5N$: C, 45.90; H, 2.75. Found: C, 45.90; H, 2.83.

The same acid may be obtained in a 40% yield by nitrating 35 g. (0.25 mole) of furylacrylic acid dissolved in 51 g. (0.5 mole) of acetic anhydride with a nitrating mixture consisting of 87.5 g. (1.4 moles) of fuming nitric acid (sp. gr. 1.5) and 140 g. (1.4 moles) of acetic anhydride, prepared after the method described for the nitration of furfural diacetate. The mixture during nitration was kept at −5°, and toward the end of the reaction a precipitate separated. The yield of acid melting at 233" was 18.3 g., and attention should again be directed to the fact that this nitro acid precipitated directly from the reaction mixture and no pyridine was required to close the ring.

Ethyl Nitrofurylacrylate, $NO_2C_4H_2OCH{=}CHCO_2C_2H_5$.—The ethyl furylacrylate

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[10] See Gilman and Hewlett, *Iowa State College J. of Science,* **4,** 27 (1929), for a recent article on the correlation of sweet taste with constitution of some furan compounds; also, Gilman and Dickey, THIS JOURNAL, 52, 2010 (1930) for a later related study.

[11] See Gilman, Brown, Wright and Hewlett, *Iowa State College J. of Science, 4,* 355 (1930), for the helpful effect of several fusions of sodium acetate on the yield of furylacrylic acid.

[12] This low yield can probably be improved in larger-sized runs. Our chief object here was to prepare some of the acid in order to confirm that obtained by direct nitration of furylacrylic acid.

was prepared in accordance with the directions of Gilman, Brown and Jones[13] and **41.5** g. (**0.25** mole) of it was nitrated after the procedure described for the nitration of furylacrylic acid. The mixture was stirred for three hours and during this time a yellow precipitate separated. When the temperature reached 0°, the reaction product was removed by filtration and washed several times with cold water. The yield of ethyl nitrofurylacrylate, melting at 123°, was **27** g. or 51%. When recrystallized from benzene, it melted at 125°.

Anal. Calcd. for $C_9H_9O_5N$: C, **51.18;** H, **4.30.** Found: C, **50.68;** H, **4.43.**

The ester is unusually stable, being quite resistant to thionyl chloride and phosphorus pentachloride. It may be hydrolyzed with 65% sulfuric acid by heating until solution is completed, to give the nitrofurylacrylic acid. The identity of this acid, like the other compounds described in this paper, was confirmed by a mixed melting-point determination, in this case with the acids obtained in the Perkin condensation and in the nitration of furylacrylic acid.

The authors gratefully acknowledge assistance from W. M. Selby for a part of the experimental work.

Summary

The first nitrofurfural has been prepared by the hydrolysis of nitrofurfural diacetate obtained by nitrating furfural diacetate. The mechanism of its formation is probably unlike that of nitrofurylacrylic acid and ethyl nitrofurylacrylate, which were obtained by direct nitration of furylacrylic acid and ethyl furylacrylate, respectively. The nitro group markedly increases the stability of the furan nucleus.

AMES, IOWA

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

THE SOLUBILITY OF ROTENONE. I. SOLUBILITY AND OPTICAL ROTATION IN CERTAIN ORGANIC SOLVENTS AT 20°

BY HOWARD A. JONES AND CHARLES M. SMITH

RECEIVED MARCH 18, 1930 PUBLISHED JUNE 6, 1930

Introduction

The root of *Derris elliptica* has long been used by the natives of the Malay Peninsula and the East Indies as a fish poison. One of the active insecticidal principles of this root is a white, crystalline material with a melting point of 163°. This material, now known as rotenone, crystallizes from alcohol in the form of six-sided plates apparently belonging to the orthorhombic system. The empirical formula $C_{23}H_{22}O_6$, now generally accepted, was first proposed by Takei and later substantiated by Butenandt. Much work has been done to determine its constitution but at present its structure is still unknown.

Rotenone is known to be practically insoluble in water, Gimlette stating its solubility to be of the order of one part in six million.[1] Numerous quali-

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[13] Gilman, Brown and Jones, *Iowa State College J. of Science*, 2, **317 (1928).**

[1] Gimlette, "Malay Poisons and Charm Cures," London, 1923, 2d ed.

tative statements as to its solubility in organic solvents are found in the literature,[2,3,4,5] but few quantitative data are available. The present investigation had as its object the finding of solvents suitable for use in extracting rotenone and for the preparation of spray mixtures. This paper treats of its solubility in some organic solvents at 20°. A later paper will deal with other solvents and with some mixed solvents, both at 20° and at higher temperatures.

Materials and General Procedure

The rotenone used consisted of several samples prepared by H. V. Claborn of this Laboratory from the root of *Derris elliptica* by extraction of the ground root with ether. The rotenone crystallizes from the concentrated extract and is purified by recrystallization from alcohol. The purity of each lot was checked by determinations of melting point and by microscopical examination. Only rotenone passing a 70-mesh sieve was used.

Twenty-one solvents, representing the more common classes of organic compounds, were used. These were, in general, of chemically pure grade, except in those cases in which a commercial grade was more readily available.

The method used for determining solubility was based on the optical activity of the compound, and was suggested by the fact that the specific rotation of rotenone was given by Kariyone, Atsumi and Shimada[6] as $[\alpha]_{\mathrm{D}}^{20}$ $-244°$ and by Ishikawa[7] as $[\alpha]_{\mathrm{D}}^{29.5}$ $-225.2°$ in benzene solution. The specific rotation of rotenone in the various solvents was first determined by the use of solutions of known concentration. Then saturated solutions were prepared, their rotations measured and the concentrations (or solubility) obtained by extrapolation.

The solvents were all tested for optical rotation, but in only one was any observed. The commercial n-butyl alcohol used was very slightly levorotatory and a corresponding correction was made in the readings. The specific gravities of the solvents and of the saturated solutions were obtained in order to permit the results to be stated in several units. All determinations were carried out in a constant-temperature room kept at 20°.

Determination of Specific Rotation.—Solutions of known concentrations were made by weighing the rotenone accurately into volumetric

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[2] Ishikawa, *Tokyo Igakkwai Zasshi*, **30**, 45 (1916); *C. A.*, **11**, 2370 (1917).

[3] Van Hasselt, *Proc. Roy. Acad. Sci. (Amsterdam)*, [Pt. 2] **13**, 688 (1911) (in English).

[4] Lenz, *Arch. Pharm.*, **249**, 298 (1911).

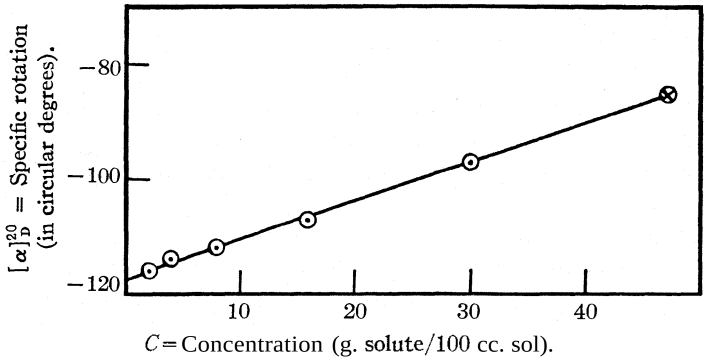
[5] Moeller and Thorns (Editors), "Real–Enzyklopadie der gesamten Pharmazie," 1905, 2d ed., Vol. IV.

[6] Kariyone, Atsumi and Shimada, *J. Pharm. Soc. (Japan)*, No. 500, 739 (1923); *C. A.*, **18**, 408 (1924).

[7] Ishikawa, *J. med. Ges. Tokio*, **31**, No. 4, 180 (1917); [abstracted by Takei, *Biochem. Z.*, **157**, 2 (1925)].

flasks and making to volume at 20° with the solvent. After considerable shaking a careful inspection was made to see whether any material remained undissolved; if so, the solution was diluted to a larger known volume, until the rotenone went into complete solution. Because of this, the concentrations are expressed as "grams of rotenone per 100 cc. of solvent" throughout the calculations. The making of these solutions also gave a rough estimate of the solubility of rotenone in each solvent.

The light used was obtained from an ordinary electric light bulb by filtration through a bichromate cell containing a solution giving an optical path equivalent to 9 mg. of $K_2Cr_2O_7$ per square centimeter. This light was therefore made up of wave lengths centering rather closely around that of the "D" line of sodium. The readings of this instrument, in Ventzke degrees, were converted to circular degrees by multiplying by the factor 0.3466. The specific rotation was then calculated by means of the formula



⊙, Observed values; ⊗, extrapolated value for saturated solution.
Equation of line $[\alpha]^{20°}_{D} = 0.67C - 117$

Fig. 1.—Specific rotation-concentration. Rotenone in chloroform at 20°.

$$[\alpha]^{20}_{D} = \frac{\text{Ventzke degrees} \times 0.3466 \times 100}{\underset{\text{(in decimeters)}}{\text{Length tube}} \times \underset{\text{(in g./100 cc. soln.)}}{\text{concentration of solution}}} \qquad (1)$$

With practically all solvents solutions of different concentrations were measured in order to determine whether there was any variation of the rotation with change in concentration. The specific rotations obtained for the various concentrations are given in Table I, Col. 3.

In those cases in which no variation with concentration was evident, the specific rotation was assumed to be a constant and its most probable value obtained by taking a weighted average of the values for specific rotation at the different concentrations, giving each the relative weight of the actual Ventzke readings.

With those solvents which gave more concentrated solutions, a definite decrease of specific rotation with increase in concentration was found.

In two other cases this same decrease was noted although the range of concentration was not as great. The results for these solvents were represented graphically by plotting the specific rotation against concentration. The variation was found to be linear within the limits of error of the measurements, and the straight line which seemed best to fit the points was drawn. The parameters of the equation for this line were obtained graphically, and from the expression obtained the value for specific rotation at any concentration may be calculated. The graph obtained for chloroform is shown in Fig. I and is typical of those obtained with the other solvents.

The final values adopted for specific rotation are given in Table I, Col. 4.

TABLE I

OPTICAL ROTATION OF ROTENONE AT 20°

(1) Solvent and sp. gr. at 20°	(2) Concn. (C) of soln. in g. of solute per 100 cc. of soln.	(3) Sp. rotation of soln. in circular degrees	(4) Sp. rota.[b] $[\alpha]_D^{20}$ in circular degrees (weighted av. or equation)
Acetone"	1	−106	−105
0.791	2	−107	
	3	−109	
	5	−103	
Acetic acid[a]	1	−131	−129
1.049	1.5	−128	
	2	−129	
Alcohol, n-butyl	0.1	−105	−105
0.811			
Alcohol, ethyl (absolute)"	0.0625	−111	−124
0.789	0.1	−121	
	0.125	−132	
Alcohol, isopropyl	0.1	−126	−126
0.786			
Alcohol, methyl[a]	0.1	−156	−156
0.791	0.2	−156	
Amyl acetate	0.75	− 92	− 93
0.867	1.4	− 93	
Benzene"	2	−230	$[\alpha]_D^{20} = 1.8C-233$
0.879	4	−225	
	8	−219	
Carbon disulfide"	1	− 96	− 96
1.263	1.5	− 99	
	2[c]	− 95	
Carbon tetrachloride[a]	0.25	−107	−108
1.594	0.375	−104	
	0.5	−111	
Chlorobenzene	4	−168	$[\alpha]_D^{20} = 1.7C-175$
1.107	8	−162	
	10	−158	

TABLE I (Concluded)

(1) Solvent and sp. gr. at 20°	(2) Concn. (C) of soln. in g. of solute per 100 cc. of soln.	(3) Sp. rotation of soln. in circular degrees	(4) Sp. rota.[b] $[\alpha]^{20}_D$ in circular degrees (weighted av. or equation)
Chloroform[a]	2	−116	$[\alpha]^{20}_D = 0.67C - 117$
1.489	4	−114	
	8	−112	
	16	−107	
	30	− 97	
s-β-Dichloro-ethyl ether[a]	1	− 85	$[\alpha]^{20}_D = 0.53C - 85$
1.208	3	− 83	
	6	− 82	
Ether, ethyl (anhydrous)[c]	0.1	−147	−136
0.714	0.25	−139	
	0.3	−130	
Ethyl acetate[a]	0.5	−106	−107
0.901	1	−106	
	1.5	−107	
	3	−107	
Ethylene chlorohydrin	2	−103	$[\alpha]^{20}_D = 0.35C - 104$
1.203	4	−102	
	7	−102	
	10	−100	
Ethylene dichloride	6	− 74	$[\alpha]^{20}_D = 0.44C - 77$
1.256	15	− 71	
	25	− 66	
n-Propyl formate	1	−108	−106
0.896	4	−106	
	5	−106	
Toluene[a]	3	−210	−209
0.866	5	−211	
	6	−206	
Trichloro-ethylene	5	−100	$[\alpha]^{20}_D = 0.77C - 104$
1.469	10	− 96	
	14	− 93	
Xylene	1	−213	$[\alpha]^{20}_D = 4.0C - 217$
0.864	2	−210	
	3	−205	

[a] Solvents of "Chemically Pure" grade. The specific gravity of each of these was obtained from the "International Critical Tables," Vol. III. All other solvents were less pure and their specific gravities were determined by pycnometer.

[b] Although the specific rotation is quoted as $[\alpha]^{20}_D$ it does not refer as accurately to the wave length of "D" light as do measurements made with strictly monochromatic sodium light.

[c] This solution is apparently supersaturated. Upon addition of more rotenone and shaking for four hours the concentration is reduced to that of the saturated solution.

An inspection of Table I shows that rotenone is levorotatory in all solvents and at all concentrations tested. In ten of the solvents the specific rotation lies between —90 and —110°. In only two is it below this, while in the remainder it is appreciably higher, with benzene and its homologs forming a rather distinct group above —200°. The specific rotation definitely decreases with increasing concentration in the six solvents in which rotenone is most soluble, and also seems to do so in two other solvents in which it is moderately soluble.

The values for specific rotation do not all have the same degree of accuracy due to the fact that in those solvents giving only low concentrations it was impossible to get large readings on the instrument. This is indicated in Table I by the smaller size of the third digit in the cases of the alcohols, ether and carbon tetrachloride. In the cases of benzene and its homologs it was evident that the rotation dispersion was not fully compensated, but this caused practically no difficulty in making the readings.

Preparation and Optical Rotation of Saturated Solutions.—In obtaining saturated solutions of rotenone in the various solvents, the following procedure was adopted. An approximately weighed amount of rotenone[8] was introduced into ordinary test-tubes of about 30-cc. capacity. The solvent was added (*25* cc. or less, depending on the amount of solid present) and the tubes tightly stoppered with cork stoppers. These tubes were placed in a shaking machine consisting of a vertical wooden disk (diameter, 16 inches) to which the tubes were held in a radial position, the disk being rotated by an electric motor at a speed of about *25* to 30 r. p. m. The shaking was continued through a period of seven hours, which trial experiments had shown to be sufficient for the attainment of equilibrium. The tubes were then removed from the shaker and allowed to stand upright overnight. In the morning the tubes were well shaken by hand and filtered directly into polariscope tubes of suitable length and the optical rotations of the clear solutions determined immediately in the saccharimeter already described. This entire operation was carried out in a constant-temperature room maintained at 20°.

At least two determinations were made with each solvent; the average results are given in Table II, Col. 4. The readings are given in Ventzke degrees, and for the sake of uniformity are calculated to a 1-decimeter tube, although in some cases longer tubes were used so that the actual reading could be made more accurately on the instrument.

Crystals Obtained from Solution.—In the preparation of saturated solutions in benzene, carbon tetrachloride and chloroform it was found that the solution could be supersaturated with rotenone but when an excess of rotenone was added an almost solid mat of needle-like crystals immediately separated. For this reason it was thought necessary to make a brief study of the crystals obtained from solutions of rotenone in some of the solvents used. To accomplish this, small amounts of rather concentrated solutions were evaporated at room temperature in a draft of air until crystallization

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[8] The relative amounts of rotenone and solvent were adjusted so that from *25* to 50% rotenone in excess of that required to saturate the solution was present, as judged from trial experiments.

TABLE II

SOLUBILITY DATA FOR ROTENONE AT 20°

(1)	(2)	(3)	(4) Optical rotation of satd. soln.		(5) Soly. at 20° (concn. of satd. soln.) in g. of rotenone		
Solvent	Sp. gr. of satd. soln. at 20°	Crystals obtd. from soln.	No. of detns.	Av. reading in Ventzke deg. for a 1-dm. tube	per 100 cc. of soln.	per 100 g. of soln.	per 100 cc. of solvent
Acetone	0.825	Hexag. and lozenge-shaped plates	3	− 20.0	6.6	8.0	6.9
Acetic acid	1.057	Needles and lath-like plates	2	− 8.8	2.4	2.2	2.4
Alcohol, *n*-butyl	0.814	Hexagonal-shaped plates	2	− 0.75	0.2	0.3	0.2
Alcohol, ethyl (absolute)	.792	Hexagonal-shaped plates	2	− .80	.2	.3	.2
Alcohol, isopropyl	.790	Hexagonal-shaped plates	2	− .55	.2	.2	.2
Alcohol, methyl	.796	Hexagonal-shaped plates	2	− 1.1	.2	.3	.2
Amyl acetate	.872	Hexagonal-shaped plates	2	− 4.3	1.6	1.8	1.6
Benzene	.908	Needles	4	− 50.4	8.0	8.8	8.5
Carbon disulfide	1.270	Hexagonal-shaped plates	3	− 4.5	1.6	1.3	1.6
Carbon tetrachloride	1.587	Fine needles	3	− 2.0	0.6	0.4	0.6
Chlorobenzene	1.127	Elongated, almost needle-like hexagons	2	− 59.4	13.5	12.0	15.1
Chloroform	1.430	Needles	4	−116.4	47.2	33.0	73.4
s-β-Dichloro-ethyl ether	1.228	Fine needles	2	− 17.6	7.5	6.1	7.9
Ether, ethyl (anhydrous)	0.721	Hexagonal-shaped plates	2	− 1.5	0.4	0.5	0.4
Ethyl acetate	.916	Lozenge-shaped plates	3	− 14.7	4.8	5.2	4.9
Ethylene chlorohydrin	1.210	Hexagonal-shaped plates	2	− 33.0	11.4	9.4	12.5
Ethylene dichloride	1.270	Needles	4	− 59.7	33.1	26.1	44.3
n-Propyl formate	0.915	Hexagonal-shaped plates	2	− 18.4	6.0	6.6	6.3
Toluene	.890	Hexagonal and lozenge-shaped plates; also elongated hexagons and needles	2	− 38.6	6.4	7.2	6.7
Trichloro-ethylene	1.447	Hexagonal and lozenge-shaped plates; also fine needles	2	− 43.3	16.5	11.4	19.0
Xylene	0.878	Hexagonal-shaped plates	2	− 19.8	3.4	3.8	3.5

occurred. These crystals were examined under the microscope and their general appearance noted. The results are given in Table II, Col. 3. It will be noted that rotenone crystallizes from the majority of these solvents in the form of hexagonal-shaped plates. In some cases, however, distinctly needle-shaped crystals were obtained.

It has been reported by Tattersfield and Roach[9] that the needle crystals obtained from benzene contain solvent of crystallization. Certain preliminary experiments made in this Laboratory substantiate this result, and indicate that some other solvents form similar crystalline products. In any such case it is, of course, the addition product which is in equilibrium with the saturated solution, but in the absence of more complete information the final results for solubility have been expressed in terms of rotenone.

Calculation of Solubility.—In the cases of those solvents showing no decided variation of specific rotation with change in concentration the calculation is fairly simple. After the optical rotation of the saturated solution has been obtained the corresponding concentration (in grams of rotenone per 100 cc. of solution) may be calculated from a rearrangement of Formula 1, the appropriate specific rotation being used.

$$\underset{(\text{g./100 cc. soln.})}{\text{Concentration}} = \frac{\text{Ventzke reading of satd. soln.} \times 0.3466 \times 100}{\text{Length tube (in dm.)} \times [\alpha]_{\text{D}}^{20}} \qquad (2)$$

In those cases in which the specific rotation was found to vary with the concentration, the concentrations of the saturated solutions were calculated from the equations given in Table I, Col. 4, for the specific rotation–concentration graph. This was done by substituting for the specific rotation its value in terms of the known Ventzke reading of the saturated solution (Table II, Col. 4) and the unknown concentration ("C"), and solving for the latter.

The values obtained from these calculations give the solubility, or concentration of the saturated solution, in terms of "grams of rotenone per 100 cc. of solution." By the use of the specific gravities of the solvent and of the saturated solution these values have been converted to "grams of rotenone per 100 g. of solution" and "grams of rotenone per 100 cc. of solvent." The solubility of rotenone, in terms of these three units, is given in Table II, Col. 5.

Discussion of Solubility Data

In general, it appears that rotenone is most soluble in the chloro products, with the exception of carbon tetrachloride. Benzene is also a good solvent, but the addition of aliphatic residues, as in toluene and xylene, seems to lower the solvent power, while the addition of chlorine, as in chlorobenzene, increases the solubility. Acetone is a fair solvent, as are also acetic acid and the three esters tested. The alcohols and ether, contrary to state-

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[9] Tattersfield and Roach, *Ann. appl. biol.*, 10, No. 1, 1 (1923).

ments found in the literature, are rather poor solvents for rotenone. However, at higher temperature their solvent powers may increase considerably. For example, it was found in trial experiments that absolute ethyl alcohol, at its boiling point, will dissolve as much as 4 g. of rotenone per 100 cc. of solution, and it is this large temperature gradient which makes it useful in the recrystallization of rotenone.

An attempt was made to determine the solubility of rotenone in certain oils by the method outlined above, but, due to extremely low solubility in some cases and to difficulties caused by high optical rotation of the solvent in other cases, the method was found to be not applicable. It may be stated with some degree of certainty, as the result of trial experiments, that the solubility of rotenone in petroleum ether, gasoline, kerosene, "Nujol" and rectified oil of turpentine is less than one-tenth of one per cent. at 20°. Rotenone, however, appears to be appreciably soluble in Menhaden fish oil and in steam-distilled pine oil.

Since this article was written an interesting reference has been brought to the attention of the authors. Geoffroy[10] in 1895 isolated from the plant *Robinia nicou* now known as *Lonchocarpus nicou* (one of the species locally called "cube"), a material which he named "nicouline." The properties of this material indicate that he was dealing with what we now know as rotenone. This is substantiated by the fact that Clark[11] has recently found rotenone in "cube" roots.

Among other properties Geoffroy made a quantitative study of the solubility of "nicouline" in various solvents and obtained values markedly higher than those given in this paper, but bearing the same general relationship to each other. The temperature at which these measurements were made is not specified and if higher than 20° might account for the higher values.

Summary

The optical rotation at 20° of rotenone in twenty-one organic solvents has been determined and found to range from -66 to $-230°$.

The solubility at 20° of rotenone has been determined in these same solvents and found to range from 0.2 to 33%.

The solubility is very low in petroleum hydrocarbons, which are used extensively for spraying purposes.

WASHINGTON, D. C.

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[10] Geoffroy, *Annales de L'Institut Colonial de Marseille*, 2, 1–80 (1895)

[11] Clark, *Science*, 70, 478 (1929).

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

ACTION OF TITANIUM TETRACHLORIDE ON DERIVATIVES OF SUGARS. II. PREPARATION OF TETRA-ACETYL-BETA-NORMAL-HEXYLGLUCOSIDE AND ITS TRANSFORMATION TO THE ALPHA FORM[1,2]

BY EUGEN PACSU

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One of the difficulties which restricts the range of synthetical operations in the sugar series may be seen in the comparative inaccessibility of glycosides of the alpha configuration. No method has hitherto been described, that is, of general applicability in preparing such derivatives and most of the methods yield a product which is greatly contaminated by the isomeric beta form or other substances. A review of the literature shows that four methods have been proposed. The earliest of these was due to Emil Fischer,[3] who heated the reducing sugar with an alcohol in the presence of hydrogen chloride. Carried out, as this procedure was, with an acid medium and at an elevated temperature, it was obviously unsuitable for use with the compound reducing sugars and it also possessed the disadvantage of yielding from the simple sugars (except in the case of mannose) an equilibrium mixture of alpha and beta glycosides. Moreover, while Fischer obtained satisfactory results with alcohols of low molecular weight, the method was not applicable when the hydroxyl group to be esterified was attached to a long aliphatic chain or was of a phenolic nature. Another means of synthesizing alpha glycosides was discovered by the present author,[4] who found that the mercaptals of various monosaccharides yield these derivatives when decomposed by mercuric chloride dissolved in the appropriate alcohol. Like the method of Fischer, however, this also is restricted to the monosaccharides in its application, because the production of the mercaptals depends upon the interaction of a reducing sugar and a thioalcohol in strongly acid solution and mercaptals of the compound sugars obviously cannot be prepared in this way because of hydrolysis. Bourquelot and his co-workers[5] studied the action of the enzyme alpha glucosidase, present in yeast, and were able to show that it is capable of synthesizing alpha glycosides from a dilute alcoholic solution of certain reducing sugars. Their observations do not appear to have been developed into a method of practical importance and the same remark may be made con-

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[1] Publication authorized by the Director of the Bureau of Standards, U. S. Department of Commerce.

[2] Part I was published in *Ber.*, 61, 1508 *(1928).*

[3] Fischer, *ibid.*, 26, 2400 (1893).

[4] Pacsu, ibid., 58, 509 (1925).

[5] Bourquelot and Verdon, *J. pharm. chim.*, [7] *8, 19* (1913).

cerning the well-known synthesis of acetylated beta glycosides by Koenigs and Knorr[6] as modified by Fischer and Mechel[7] for the preparation of the alpha isomerides. The latter authors in some cases used quinoline, instead of silver oxide or carbonate, to neutralize the hydrobromic acid liberated when the aceto-halogeno sugar reacted with an alcohol and under these conditions obtained a mixture of both forms. The difficulty of separating the alpha and beta isomers seems to be responsible for the fact that the modified method has not come into general use.

A recent article by the present writer[8] described some experiments which were made with glucose β-penta-acetate and with tetra-acetyl-β-methylglucoside. These were allowed to interact, respectively, under various conditions of temperature and time, with equimolecular quantities of stannic chloride in chloroform and it was found that this reagent was capable of slowly transforming both the β-penta-acetate and the tetra-acetyl-β-methylglucoside into the corresponding alpha forms. Part 1[2] of the present research describes the improvement that was observed when titanium tetrachloride was substituted for the stannic salt first used. Although the new reagent far excelled the old in promoting the same transformation, the mechanism of the reaction appeared to be essentially different in the two cases, for a yellow addition compound that was insoluble in chloroform was immediately produced when titanium tetrachloride was, added to the solution of the glucose derivative. This phenomenon did not occur when stannic chloride was employed. Tetra-acetyl-a-methylglucoside was readily obtained in excellent yield by the improved method but it was worthy of note that glucose a-penta-acetate and similar substances underwent a secondary change and were smoothly transformed to the corresponding a-acetochloro sugars. Indeed, the use of titanium tetrachloride furnished in this way a means of preparing the latter derivatives that is as convenient as any that were previously known. This secondary reaction was also brought about by stannic chloride, though with much greater difficulty.

In view of the importance of acquiring a general method for preparing alpha glycosides of the reducing sugars, and having regard to the promising nature of the experiments of which a résumé has been given, the action of titanium tetrachloride upon the fully acetylated sugars and beta glycosides has been made the subject of further study. It seems necessary to submit suitable derivatives of the mono- and disaccharides to the action of the inorganic chloride in order to test the generality of the reaction. The present article forms a part of this general plan of research and describes the synthesis of tetra-acetyl-a-n-hexylglucoside from tetra-acetyl-β-*n*-

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[6] Koenigs and Knorr, Ber., 34, 957 (1901).

[7] Fischer and Mechel, *ibid.*, 49, 2814 (1916).

[8] Pacsu, *ibid.*, 61, 137 (1928).

hexylglucoside by means of titanium tetrachloride. As the sugar residue in this particular glucoside is attached to an unbranched chain of six carbon atoms, the glucosidic linkage is probably somewhat similar in its reactivity to that which occurs in many disaccharides and the investigation may be regarded as a preliminary step in the development of this field.

Koenigs and Knorr's method was used to prepare tetra-acetyl-β-*n*-hexylglucoside from acetobromoglucose and n-hexyl alcohol. This acetylated glucoside, which is a new substance, is a crystalline solid melting at 51.5° and having a specific levo-rotation in chloroform of $[\alpha]_D^{20}$ $-19.9°$ when pure. Although stable to Fehling's solution, it is very easily hydrolyzed by dilute acids and even by steam when in a neutral medium. The fatty character of the aglycon (*i. e.*, non-sugar component) dominated its physical properties and it quickly dissolved in all the common organic solvents, including even petroleum ether. It was insoluble in water.

In order to obtain the alpha form of tetra-acetyl-*n*-hexylglucoside, it was sufficient to heat the pure beta isomer with an equimolecular quantity of titanium tetrachloride in the presence of chloroform, as described in the experimental part. Control of the duration of heating was found to be quite important. When seventy-five minutes had elapsed, ice water was used to decompose the yellow solution. Both the water and the chloroform immediately became colorless and tetra-acetyl-α-*n*-hexylglucoside was recovered from the latter solvent by standard processes as a crystalline solid of m. p. 61° and with a specific dextro-rotation of $[\alpha]_D^{20}$ $+116.5°$ in chloroform, after purification. The yield was 83% of the theoretical. The substance resembled the beta isomer in its solubilities and in its ready hydrolysis.

Although analysis showed that the new compound possesses the expected composition, the possibility remained that a change in the ring structure or stereochemical configuration, accompanied by a wandering of the acetyl groups, might have occurred during its preparation from tetra-acetyl-β-*n*-hexylglucoside. This question was examined in the following way. Hudson[9] has shown that it is permissible to regard the molecular rotation of a pair of acetylated glucosides possessing the same oxide bridge linking as composed of two quantities A and B, where A is the rotation due to the first asymmetric carbon atom of the sugar chain and B refers to the remainder of the glucose molecule. The latter portion, B, is independent of the particular pair of acetylated glucosides considered and has the value $B = +20{,}350$ in chloroform.[10] Writing the molecular rotation of the beta form of tetra-acetyl-n-hexylglucoside (mol. wt. 432) as $-A + B = (-19.9)(432) = -8597$ and subtracting the value of B gives $A = +28{,}947$ and hence $A + B = +49{,}297$. The last figure is the calculated molecular

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[9] **Hudson,** THIS JOURNAL, **31,** 66 (1909).

[10] Hudson and Dale, *ibid.*, 37, *1264* **(1915).**

rotation of a tetra-acetyl-a-n-hexylglucoside similar in ring structure to the original beta form. The calculated specific rotation $[\alpha]_D$ of the compound is accordingly $49{,}297/432 = +114°$ in chloroform. The close agreement between this computed value and that found by experiment for tetra-acetyl-a-n-hexylglucoside (+116.6°) furnishes definite proof that the alpha and beta forms of tetra-acetyl-*n*-hexylglucoside have like ring structures and, further, that this ring is the same as the ring of the alpha and beta forms of normal tetra-acetyl-methylglucoside. The last conclusion follows from the fact that the value of B used in the calculation is derived from the rotations of the normal tetra-acetyl-methylglucosides. It has recently been shown by Hudson[11] that the ring here referred to is of the 1,5 type.

Experimental

Preparation of **Tetra-acetyl-β-*n*-hexylglucoside.**—A solution of 30 g. of acetobromoglucose and 50 g. of pure n-hexyl alcohol in 500 cc. of absolute ether was shaken for five hours at room temperature with 18 g. of freshly prepared dry silver oxide. After the removal of the insoluble silver salts, the ethereal solution was evaporated under reduced pressure to a sirup, which was submitted to a steam distillation. The operation was cut short at the end of three hours, although the presence of a few oily drops in the distillate falling from the condenser showed that the excess of insoluble hexyl alcohol had not entirely passed into the receiver. The slight instability of the glucoside under the experimental conditions rendered this course advisable. A yellow sirup now lay underneath the water in the distilling flask. It was taken up in 250 cc. of ether and the solution was washed with dilute aqueous potassium bicarbonate solution and then twice with water, after which it was dried over anhydrous calcium chloride and evaporated under diminished pressure. The residue quickly crystallized and yielded about 15 g. of tetra-**acetyl-@-n-hexylglucoside,** Decolorizing carbon, used at room temperature, withdrew all the coloring matter from a solution of the crude product in petroleum ether and the acetylated glucoside then crystallized from the colorless filtrate on standing at 0° in the form of long prismatic needles of m. p. 51.5" and of specific levo-rotation $[\alpha]_D^{20}$ $-19.3°$ in chloroform. After a second recrystallization from petroleum ether the substance showed $[\alpha]_D^{20}$ $-19.9°$, which is accepted as the rotation of the pure substance (0.4311 g. subs. in 25 cc. of $CHCl_3$ solution rotated 0.685" to the left in a 2-dm. tube).

In an acetyl estimation, made by the method of Kunz,[12] 0.4840 g. was dissolved in 50 cc. of pure acetone to which 103.8 cc. of 0.1 *N* potassium hydroxide was subsequently added. The acetylated glucoside neutralized 44.8 cc. of decinormal alkali, in excellent agreement with the calculated value of 44.78 cc.

Tetra-acetyl-α-*n*-hexylglucoside from **Tetra-acetyl-β-*n*-hexylglucoside.**—A solution of 1.9 g. of titanium tetrachloride in 50 cc. of absolute chloroform[13] was added to 4.3 g. of tetra-acetyl-β-*n*-hexylglucoside dissolved in 100 cc. of the same solvent. This mixture immediately became lemon-yellow in color although it remained clear, from which fact it is inferred that the addition product of this acetylated glucoside with titanium chloride is more soluble in chloroform than the compounds previously studied

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[11] Hudson, THIS JOURNAL, 52, 1680 (1930).

[12] Kunz and Hudson, *ibid.*, 48, 1982 (1926).

[13] The chloroform used in this and the following experiments was pure U. S. P. chloroform which had been twice extracted with water, dried with anhydrous calcium chloride and distilled from phosphorus pentoxide.

(see the introduction). The solution was boiled gently for seventy-five minutes on a water-bath in a flask closed by a reflux condenser provided with a calcium chloride drying tube. No noticeable color change occurred during this operation and when it was over the liquid was poured into a separatory funnel containing ice water. After shaking, both the chloroform and water layers became colorless. The chloroform solution was washed with a dilute potassium bicarbonate solution and then thrice with water, after which it was dried with calcium chloride. Tetra-acetyl-a-n-hexylglucoside remained in the organic solvent and was isolated by concentrating the solution under reduced pressure to a sirup, which was dissolved in cold petroleum ether and purified with carbon at room temperature. The colorless solution was then concentrated under reduced pressure to a sirup, which soon crystallized when kept in the ice box and yielded after one day 3.6 *g.* of the fairly pure glucoside acetate. The recrystallization from about 100 cc. of petroleum ether in the ice box occupied several days and yielded 3.2 g. of long prismatic needles, melting sharply at 61° and having a specific dextrorotation in chloroform of $[\alpha]_D^{20}$ +116.6° (0.7345 *g.* in 25 cc. of $CHCl_3$ solution rotated 6.85° to the right in a 2-dm. tube). A second recrystallization from petroleum ether caused no significant change in this value of the specific rotation, which is accordingly accepted as correct for tetra-acetyl-a-n-hexylglucoside in chloroform solution.

An acetyl estimation was carried out by the method previously indicated, allowing three hours for the reaction; 0.4762 g. of the substance required 44.3 cc. of 0.1 N potassium hydroxide whereas the value calculated for tetra-acetyl-n-hexylglucoside is 44.1 cc.

The author expresses his thanks to the International Education Board, whose support has made this investigation possible, and also wishes to thank Dr. C. S. Hudson for his helpful suggestions.

Summary

Tetra-acetyl-β-n-hexylglucoside, which has not been described before, was found to be a crystalline substance melting at 51.5' and having a specific levo-rotation in chloroform of $[\alpha]_D^{20}$ −19.9'. Under the influence of titanium tetrachloride in chloroform solution the substance was readily isomerized to the alpha form, which was isolated in 83% yield as a crystalline solid, m. p. 61° and $[\alpha]_D^{20}$ +116.6° in chloroform.

It follows that the action of titanium chloride in promoting the transformation of acetylated beta glycosides to their alpha isomers is not inhibited by the presence of a straight chain of six carbon atoms in the non-glucosidic portion of the molecule. Indeed, the hexylglucoside acetate is rearranged even more rapidly than the methylglucoside acetate. The sum of the rotations of the alpha and beta forms of tetra-acetyl-n-hexylglucoside conforms with Hudson's second isorotation rule and the rotation of either form may be calculated fairly accurately from that of the other, in conjunction with the rotations of the alpha and beta forms of tetra-acetyl-methylglucoside. The rotations of the two new substances thus show that they possess the same oxidic ring and that this ring is the ring of the known tetra-acetyl-methylglucosides, which has been found recently by Hudson to be of the 1,5 type.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

ACTION OF TITANIUM TETRACHLORIDE ON DERIVATIVES OF SUGARS. III. TRANSFORMATION OF TETRA-ACETYL-BETA-CYCLOHEXYLGLUCOSIDE TO THE ALPHA FORM AND THE PREPARATION OF ALPHA-CYCLOHEXYLGLUCOSIDE[1,2]

BY EUGEN PACSU

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In the preceding article the employment of titanium tetrachloride for the synthesis of acetylated alpha glycosides was extended from the case of a-methylglucoside tetra-acetate, previously studied,[3] to that of tetra-acetyl-a-n-hexylglucoside. Cyclohexylglucoside may be regarded as very similar to the same derivative of *n*-hexyl alcohol, indeed, as having been formed from it by the removal of one hydrogen atom from each end of the carbon chain and closure of the ring by the valences so set free. On the other hand, cyclohexanol is the simplest member of the hydro-aromatic alcohols, the beta glycosides of many of which are known, while only one representative of the corresponding alpha forms (α-*l*-menthyl-*d*-glucoside)[4] has yet been prepared. The present paper describes the rearrangement of tetra-acetyl-β-cyclohexylglucoside to tetra-acetyl-a-cyclohexylglucoside by means of titanium tetrachloride in chloroform, the isolation of the pure substance and its conversion to the alpha glucoside by de-acetylation.

Having prepared the acetylated beta glucoside by the directions of Fischer and Helferich[5] but on a somewhat larger scale, the pure compound was found to melt at 120–121° and to have a specific rotation of $[\alpha]^{20}_{\mathrm{D}}$ $-23.8°$ in chloroform; the values found by the former workers are m. p. 120–121° and $[\alpha]^{22}_{\mathrm{D}}$ $-29.74°$ in alcohol. As was expected, titanium chloride readily rearranged the compound to tetra-acetyl-α-cyclohexylglucoside, but trial experiments showed that it was very necessary to restrict the action of the reagent closely to seventy-five minutes under the conditions employed. Unless this was done, the golden yellow color of the chloroform solution quickly changed to deep red and the product decomposed. Pure crystalline tetra-acetyl-a-cyclohexylglucoside has a low melting point, 40–41°, a specific rotation of $[\alpha]^{20}_{\mathrm{D}}$ $+121.7'$ in chloroform and is easily distinguished from the beta isomer by its ready solubility in petroleum ether, in which solvent the beta form is nearly insoluble.

As has been mentioned, relatively few alpha glucosides are available for

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[1] Publication authorized by the Director of the Bureau of Standards, U. S. Department of Commerce.

[2] Part II was published in THIS JOURNAL, 52, 2563 (1930).

[3] Pacsu, *Ber.*, 61, 1508 (1928).

[4] Fischer and Bergmann, *ibid.*, 50, 711 (1917).

[5] Fischer and Helferich, ***Ann.*, 383,** 68 (1911).

study and the opportunity was therefore taken to de-acetylate tetra-acetyl-α-cyclohexylglucoside and so add another member to the series. The new compound, a-cyclohexylglucoside, crystallized from acetone, melted at 126° and had a specific dextro-rotation in aqueous solution of $[\alpha]_D^{20}$ +133.2° after careful purification. It was very bitter in taste.

In order to show that the action of titanium chloride on tetra-acetyl-β-cyclohexylglucoside was restricted to the terminal asymmetric carbon atom of the glucosidic chain, the specific rotations of a-cyclohexylglucoside and its tetra-acetate were calculated from those of the corresponding beta isomers by the second isorotation rule of Hudson as described in detail in Part II for a similar case. The data for the comparisons are recorded in the following table, those for β-cyclohexylglucoside being quoted from Fischer and Helferich. Let it be assumed that the ring of β-cyclohexylglucoside is 1,5, as in the methylglucosides, and that the second rule of isorotation holds for the new glucosides. The value of B is obtained from Riiber's[6] recent measurements of the rotations of the methylglucosides ($[M]_D$ = 30,830 and −6630) as (30,830 − 6600)/2 = 12,100, and the value of A is then obtained from the rotation of β-cyclohexylglucoside as 12,100 + 10,850 = 22,950. The rotation of the a-cyclohexylglucoside is then calculated to be $[\alpha]_D = (12{,}100 + 22{,}950)/262 = 134$, in excellent agreement with the observed value (133.2). Similarly, in the case of the tetra-acetates of these glucosides, B' = 20,350' and A' = 20,350 + 10,230 = 30,580; the rotation of tetra-acetyl-a-cyclohexylglucoside is then calculated to be $[\alpha]_D = (20{,}350 + 30{,}580)/430 = 118$, which is quite near the observed value (121.7). These two agreements between theory and observation prove that the cyclohexylglucosides and their tetra-acetates possess the same ring as the methylglucosides, namely, 1,5, as allocated recently by Hudson.[8]

TABLE I

ROTATIONS OF THE PURE ALPHA AND BETA CYCLOHEXYLGLUCOSIDES (MOL. WT. *262)* AND THEIR TETRA-ACETATES (MOL. WT. *430)*

Compounds	M p., °C.	$[\alpha]_D$	$[M]_D$	Solvent
a-Cyclohexyl-d-glucoside	*126*	*133.2*	$+34{,}900 = +A + B$	H_2O
β-Cyclohexyl-*d*-glucoside	*133–137*	*−41.4*	$-10{,}850 = -A + B$	H_2O
Tetra-acetates of				
a-Cyclohexyl-d-glucoside	*4041*	*121.7*	$+52{,}330 = +A' + B'$	$CHCl_3$
β-Cyclohexyl-*d*-glucoside	*120–121*	*−23.8*	$-10{,}230 = -A' + B'$	$CHCl_3$

Experimental

Tetra-acetyl-β-cyclohexylglucoside.—Sixty grams of acetobromoglucose, *800* **cc.** of absolute ether, *200* g. of pure cyclohexanol and *30* **g.** of dry freshly prepared silver oxide were allowed to react as described by Fischer and Helferich.[5] The crude producr

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[6] Riiber, ***Ber.*, 57**, *1797 (1924).*

[7] Hudson and Dale, THIS JOURNAL, 37, *1264* (1915).

[8] Hudson, ***ibid.*, 52**, *1680 (1930).*

weighed 42 g. and was twice recrystallized from hot alcohol before its rotation became constant at the value $[\alpha]_D^{20}$ $-23.8'$ in chloroform (1.326 g. in 25 cc. of solution gave a reading of 2.53° to the left in a 2-dm. tube). This determination, together with the melting point of 120–121°, was accepted as referring to the pure compound.

Transformation of Tetra-acetyl-β-cyclohexylglucoside to the New Isomeric Alpha Form.—A solution of 13.5 g. of titanium tetrachloride in absolute chloroform[9] was added to a solution of 30 g. of tetra-acetyl-β-cyclohexylglucoside in 350 cc. of the same solvent at room temperature, whereupon the mixture assumed a golden yellow color and became perceptibly warm. The reaction was hastened by boiling the solution gently under a reflux condenser in the absence of atmospheric moisture, and experience showed that the transformation was practically complete after seventy-five minutes. Ice water removed the inorganic constituents from the cooled liquid and also caused its deep yellow color instantly to disappear, leaving a colorless chloroform solution which was washed with aqueous potassium bicarbonate and thrice with water and then dried over anhydrous calcium chloride and evaporated under reduced pressure. The residual sirup (29 g.) soon crystallized and the crude acetylated glucoside which was extracted from it by cold petroleum ether was allowed to crystallize in the ice box from the extract after the latter had been filtered through carbon. Four days later the long needles or star-like clusters of stout prisms were isolated, preferably in a cool room on account of their low melting point, and were stored in an evacuated desiccator. The yield of the once recrystallized substance was 80% of the theoretical (24 g.). Its specific rotation was $[\alpha]_D^{20}$ $+121.7°$ in pure chloroform (0.6561 g. in 25 cc. of solution rotated 6.39' to the right in a 2-dm. tube) and a second recrystallization did not change this value. The pure substance melts at 40–41°. It is stable to Fehling's solution and is soluble in most organic solvents, including petroleum ether, but is insoluble in water.

In an acetyl estimation, carried out by Kunz's method,[10] 0.528 g. was equivalent to 23.8 cc. of 0.2 *N* potassium hydroxide solution, the reaction time being two hours, in comparison with 24.5 cc. calculated for tetra-acetyl-cyclohexylglucoside.

α-Cyclohexylglucoside.—The method of Zemplén[11] was used to de-acetylate tetra-acetyl-a-cyclohexylglucoside. One hundred cc. of absolute methyl alcohol in which 1.5 g. of metallic sodium had been dissolved was added to a solution of 18 g. of the acetylated glucoside in 250 cc. of absolute chloroform. Both solutions were well cooled in an ice and salt bath prior to their mixing and the temperature of the mixture did not rise much above 0° for the first half hour. Water (15 cc.) was then added and the liquid was allowed to stand for another half hour before the addition of a considerable quantity of water. The chloroform layer, which proved to be without optical rotation, was rejected but the aqueous portion which contained the product was made slightly acid with acetic acid and evaporated under reduced pressure to a sirup, which was extracted repeatedly with acetone. The substance was isolated in crystalline form and with a 90% yield by concentrating the acetone solution after decolorizing it with carbon. After two recrystallizations from acetone, the specific rotation of the glucoside was $[\alpha]_D^{20}$ $+131.7°$ in water. After the third, $[\alpha]_D^{20}$ was $+133.2°$ (0.3622 g. in 25 cc. rotated 3.86° to the right in a 2-dm. tube) while the second fraction which separated from the solution had $[\alpha]_D^{20}$ $+132.9°$. A specific rotation of $[\alpha]_D^{20}$ $+133.2°$ was accordingly accepted as correct for an aqueous solution of α-cyclohexylglucoside. The same specimen was carefully dried in a vacuum before analysis.

Anal. Subs., 0.1486: CO_2, 0.2987; H_2O, 0.1138. Calcd. for $C_{12}H_{22}O_6$ (cyclohexylglucoside): C, 54.92; H, 8.45. Found: C, 54.82; H, 8.56.

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[9] For preparation of the chloroform, see note 13 to Part II.

[10] Kunz and Hudson, THIS JOURNAL, 48, 1982 (1926).

[11] Zemplén, *Ber.*, 59, 1254 (1926).

The new glucoside, which crystallized as small, stout prisms or as thick prismatic needles, had a melting point of 125–126° and was very soluble in cold water, acetone or alcohol, rather less so in hot ethyl acetate and benzene, but was insoluble in chloroform, ether and petroleum ether. It failed to reduce Fehling's solution. It is very bitter in taste.

The author expresses his thanks to the International Education Board, whose support has made this investigation possible, and also wishes to thank Dr. C. S. Hudson for his helpful suggestions.

Summary

Tetra-acetyl-β-cyclohexylglucoside was readily rearranged by titanium tetrachloride to the isomeric alpha form and the use of this inorganic chloride in promoting such a transformation has therefore been extended to the acetylated glucoside of a hydro-aromatic alcohol. α-Cyclohexylglucoside was prepared from the acetate by de-acetylation. The observed rotations of the new α-glucoside and its acetate agree well with values calculated by Hudson's second isorotation rule and the agreement shows that the oxidic ring in the cyclohexylglucosides and their acetates is the same as the ring of the normal methylglucosides, namely, 1,5, as recently allocated by Hudson.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

ACTION OF TITANIUM TETRACHLORIDE ON DERIVATIVES OF SUGARS. IV. TRANSFORMATION OF HEPTA-ACETYL-BETA-METHYLCELLOBIOSIDE TO THE ALPHA FORM AND THE PREPARATION OF ALPHA-METHYLCELLOBIOSIDE[1]

BY EUGEN PACSU

RECEIVED MARCH 31, 1930 PUBLISHED JUNE 6, 1930

It has been shown in the previous articles that the preparation of alpha glucosides from the respective beta compounds by the action of titanium tetrachloride can be accomplished with various types of beta glucosides. Transformations were obtained where the aglycon (*i. e.*, non-sugar component) of the glucoside was a single methyl group, an unbranched chain of six carbon atoms or a hydrogenated benzene ring. The mechanism of the reaction appears to consist in the formation of a halochromic double compound of titanium tetrachloride with the fully acetylated beta glucoside in absolute chloroform solution and the rapid isomerization of this compound on heating the solution, with the resulting production of acetylated alpha glucosides. All the transformations have been made so far with derivatives of only one sugar, d-glucose, a representative of the monosaccharides; the

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[1] Publication authorized by the Director of the Bureau of Standards. Part III was published in THIS JOURNAL, 52, **2568** (1930).

extension of the method to the production of alpha glycosides of the reducing disaccharides from their beta forms, which are easily accessible through the Koenigs–Knorr synthesis, was next undertaken and the results in the case of methylcellobioside, where the alpha form has now been synthesized, are reported in this article.

Beta-hepta-acetyl-methylcellobioside, first described by Hudson and Sayre,[2] was prepared from cellobiose octa-acetate through the acetobromo derivative. Certain modifications of their directions gave an increased yield, as will be described in the experimental part. Titanium chloride caused beta-hepta-acetyl-methylcellobioside to rearrange in chloroform solution in the course of six hours' heating and the main product was the alpha form of this substance, of m. p. 185° and $[\alpha]^{20}_{\mathrm{D}}$ +55.7° in chloroform, when pure. Consideration of the rotatory powers, as will presently be discussed, shows that this substance has the same ring structure as the original beta form. There was also isolated from the reaction mixture a small quantity of a second crystalline substance, showing a sharp melting point of 174° and $[\alpha]^{20}_{\mathrm{D}}$ +23.8° in chloroform. Its hydrolysis by acids yielded d-glucose as the sole sugar component and it thus appears to be a derivative either of cellobiose or some other di-glucose disaccharide. The de-acetylation of alpha-hepta-acetyl-methylcellobioside gave a good yield of crystalline alpha-methylcellobioside, of m. p. 144–145 and $[\alpha]^{20}_{\mathrm{D}}$ +96.8° in water, when pure.

The rotations of the alpha and beta forms of methylcellobioside and their hepta-acetates may be compared through Hudson's isorotation rule in the way that has been indicated in the two preceding articles.

TABLE I

ROTATIONS OF THE ALPHA AND BETA FORMS OF METHYLCELLOBIOSIDE (MOL. WT. 356) AND THEIR HEPTA-ACETATES (MOL. WT. 650)

Substance	M. p., °C.	$[\alpha]_{\mathrm{D}}$	$[M]_{\mathrm{D}}$	Solvent
α-Methyl cellobioside	144–145	+96.8	$+34{,}460 = +A + B'$	H_2O
β-Methyl cellobioside	193	−18.9	$-6{,}730 = -A' + B'$	H_2O
Hepta-acetates of				
α-Methyl cellobioside	185	+55.7	$+36{,}200 = +A + B$	$CHCl_3$
β-Methyl cellobioside	187	−25.4	$-13{,}260 = -A + B$	$CHCl_3$

Hudson and Johnson[3] have shown that the value of B, which is obtained from the rotation of the alpha and beta forms of cellobiose octa-acetate, is +8,800 and from this value it was predicted by Hudson and Sayre[2] fifteen years ago that the specific rotations of the alpha and beta forms of hepta-acetyl-methylcellobioside in chloroform would be +56 and —28, respectively. They synthesized the beta form and its rotation (—25.4) agreed satisfactorily with the calculated value. The alpha form could not

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[2] Hudson and Sayre, THIS JOURNAL, 38, 1867 (1916).

[3] Hudson and Johnson, *ibid.*, 37, 1278 (1915).

be made at that time because of the lack of a suitable method. The substance has now been synthesized and its rotation (+55.7) agrees closely with their calculation. The agreement proves that the primary ring structure of the methylcellobioside hepta-acetate is the same as that of alpha and beta forms of cellobiose octa-acetate, since the value of B that is used in the calculations was obtained from the rotations of the latter substances. The value of A from these acetylated methylcellobiosides is $(36{,}200 + 13{,}260)/2 = 24{,}730$, which is in good agreement with previous measurements of this value by Hudson and Dale[4] from the rotations of the acetylated methylglucosides, galactosides and xylosides. The value of A' from the methylcellobiosides is $(34{,}460 + 6730)/2 = 20{,}595$, in comparison with the average value of about 18,500 that was found by Hudson[5] from the rotations of the methylglucosides, galactosides, xylosides and arabinosides. The difference corresponds to about 6° in the specific rotation of the methylcellobiosides. The value of B' is $(34{,}460 - 6730)/2 = 13{,}865$; this is the first measurement of the rotation of the cellobioside chain. If one now combines it with the rotation of beta-cellobiose ($B' - a_{OH} = 5470$) there results $a_{OH} = 8395$, in good agreement with the value of a_{OH} from the glucose series (8440). It is evident from these agreements that all these substances of the cellobiose series possess the same kind of primary ring, which has been shown by Hudson[6] to be of the 1,5 type.

Experimental

Preparation of Alpha-Acetobromocellobiose and Beta-Methylcellobioside Hepta-acetate.—Forty grams of cellobiose octa-acetate was digested with 100 cc. of glacial acetic acid for a few minutes on the water-bath and the mixture was then cooled to 20° and 20 g. of acetic anhydride was added, followed by 130 g. of a solution of hydrobromic acid in glacial acetic acid, prepared by saturation with hydrogen bromide gas at 0°. The octa-acetate slowly dissolved during one and one-half hours at room temperature and the mixture was then kept overnight in the ice box. In the morning the crystalline mass was shaken with 2 liters of water and ice and some chloroform. The chloroform layer was washed with ice-cold dilute potassium bicarbonate solution, then several times with cold water and dried with calcium chloride. It was decolorized with activated carbon and concentrated to 100 cc. under reduced pressure. On the addition of 200 cc. of ether, 39.2 g. of alpha-acetobromocellobiose crystallized immediately; yield, 95% of the theoretical.

A solution of the acetobromocellobiose in 500 cc. of methyl alcohol was shaken for a few minutes with 25 g. of freshly prepared silver carbonate and then gently refluxed on the steam-bath, with frequent shaking, during one hour. The hot solution was filtered by suction through a layer of decolorizing carbon, which was then washed with hot methyl alcohol. The filtrate crystallized quickly on cooling and the crystals were washed with methyl alcohol followed by ether. A second crop was obtained from the mother liquor and the total yield was 34.7 g. (95% of the theoretical) of beta-methylcellobioside hepta-acetate. The product was recrystallized once from 40% methyl

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[4] Hudson and Dale, This Journal, 40, 997 (1918).

[5] Hudson, *ibid.*, 47, 268 (1925).

[6] Hudson, *ibid.*, 52, 1707 (1930).

alcohol; yield, 32.4 g. of substance of $[\alpha]_D$ −24.0 in chloroform. The value found by Hudson and Sayre is −25.4.

Transformation of Beta-Methylcellobioside Hepta-acetate to the Isomeric Alpha Form.—On mixing a solution of 6 g. of titanium tetrachloride in 50 cc. of absolute[7] chloroform with one of 20 g. of beta-methylcellobioside hepta-acetate in 300 cc. of the same solvent, a lemon yellow amorphous halochromic compound immediately separated but rapidly redissolved on shaking. The solution was gently refluxed for six hours with exclusion of moisture by a calcium chloride tube; the color slowly changed to grayish brown. After the usual treatment with ice water, potassium bicarbonate solution, etc., the dextrorotation of the slightly colored chloroform solution corresponded to about $[\alpha]_D$ 50 for the solute. Concentration of the solution under reduced pressure yielded a thick sirup which soon crystallized; the mass was dissolved in 250 cc. of hot 95% alcohol and on cooling there separated globular masses of crystals (10.5 g.) showing $[\alpha]_D$ 45.8 in chloroform. The material is a mixture and by successive recrystallizations from absolute alcohol a small quantity of a substance was obtained of sharp melting point at 174° and $[\alpha]^{20}_D$ 23.8 (0.4537 g. in 25 cc. of chloroform solution rotated 0.865 to the right in a 2-dm. tube), which did not change on further recrystallization. This appears to be a by-product of the reaction, as its rotation indicates that it is not the expected alpha isomer; since its hydrolysis by acids yields glucose as the sole sugar, it seems to be a derivative of cellobiose or of some similar di-glucose disaccharide which has been produced from cellobiose. It will be investigated further. The mother liquor from which the 10.5 g. of crystals, previously mentioned, had separated was kept for one day in the ice box and 5 g. of long flexible needles separated, showing $[\alpha]^{20}_D$ 54.4 and after one recrystallization 55.7 (0.303 g. in 25 cc. of chloroform solution rotated 1.35 to the right in a 2-dm. tube), a value which was not changed by two further recrystallizations. The rotation of this substance, its analysis and de-acetylation to give what is evidently alpha-methylcellobioside (as shown by the rotation and analysis of the latter) show that it is the expected alpha-methylcellobioside hepta-acetate, and it was obtained in about 25% yield from its beta isomer. Its melting point is 185° and in its solubility in organic solvents it closely resembles the beta isomer except that it is more soluble in absolute alcohol.

An acetyl estimation by the method of Kunz[8] corresponded with the composition of a hepta-acetate of methylcellobioside; 0.5126 g. of substance in acetone solution at 0° neutralized 55.4 cc. of 0.1 N potassium hydroxide in comparison with the calculated value, 55.17 cc.

Preparation of Alpha-Methylcellobioside by the De-acetylation of its Hepta-acetate.—The acetate was de-acetylated by Zemplén's[9] method, with slight modifications. Forty cubic centimeters of a 0.5 N solution of sodium methylate in absolute methyl alcohol was slowly added from a buret to an ice cold solution of 8.3 g. of pure alpha-methylcellobioside hepta-acetate in 60 cc. of absolute chloroform and the mixture was kept for one hour in an ice and salt bath. The sodium methylate addition product separated as a gelatinous mass. Ten cubic centimeters of water were then added and after fifteen minutes at room temperature 200 cc. of 0.1 N sulfuric acid was added to convert the sodium acetate to sulfate. The water layer was then concentrated under reduced pressure to a thin sirup which was taken up in absolute alcohol and the sodium sulfate filtered off. The filtrate was concentrated similarly to dryness, the residue was extracted with hot absolute alcohol and the solution was decolorized with carbon. After one day it yielded 4.15 g. of microscopic needles (92% of the theoretical) showing

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[7] Prepared as described in Footnote 13, Part II.

[8] Kunz and Hudson, THIS JOURNAL. 48, 1892 (1926).

[9] Zemplén, *Ber.*, 59, 1254 (1926).

$[\alpha]^{20}_{D}$ 96.6 in water (0.244 g. of substance in 25 cc. of chloroform solution rotated 1.73 to the right in a 2-dm. tube). Successive recrystallizations gave the values 97.1, 96.8 and 96.7 and the value 96.8 is accepted for pure **alpha-methylcellobioside.** The pure substance melts at 144–145°, tastes faintly sweet and does not reduce Fehling's solution. The crystals which had been dried in a desiccator at room temperature did not lose weight appreciably when kept at 110° in vacuo for four hours.

Anal. Subs, 0.155: CO_2, 0 249; H_2O, 0 096. Calcd. for $C_{13}H_{24}O_{11}$: C,. 43.79; H, 6.79. Found: C, 43.5; H, 6.93.

The author expresses his thanks to the International Education Board for the grant of a fellowship which enabled him to carry out this investigation. He also thanks Dr. C. S. Hudson for helpful suggestions.

Summary

Alpha-methylcellobioside has been synthesized through the transformation of the known beta-methylcellobioside hepta-acetate to its new alpha isomer by the action of titanium tetrachloride, followed by de-acetylation. The rotations of the various substances agree in first approximation with the values predicted by Hudson's rules of isorotation and the results indicate that the primary ring in all of them is of the 1,5 type. The titanium tetrachloride transformation yielded along with alpha-methylcellobioside hepta-acetate a second crystalline substance which showed in a pure condition $[\alpha]_D$ 23.8 in chloroform and m. p. 174; it is being studied further.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A SYNTHESIS OF METHIONINE

BY WALLACE WINDUS AND C. S. MARVEL

RECEIVED APRIL 23, 1930 PUBLISHED JUNE 6, 1930

Several years ago Mueller[1] isolated from the hydrolytic products of casein a new amino acid which contained sulfur. He determined its composition and prepared some derivatives. More recently Barger and Coyne[2] have demonstrated that this amino acid was γ-methylthiol-α-amino-*n*-butyric acid and succeeded in synthesizing the racemic compound from methylthiolpropionaldehyde by use of the Zelinsky–Stadnikoff modification of the Strecker method. The yields were not very satisfactory and the starting materials are not readily available.

A new synthesis of this interesting amino acid has been accomplished which seems to be more satisfactory as a method of preparation than the original method of Barger and Coyne. The reactions involved are represented by the following outline

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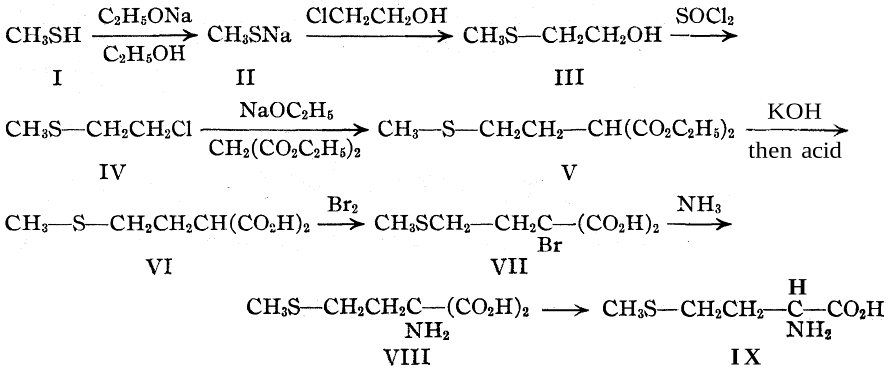
[1] Mueller, *J. Biol. Chem.*, *56*, 167 (1923).

[2] Barger and Coyne, *Biochem. J.*, 22, 1417 (1928).



$$\underset{\text{I}}{CH_3SH} \xrightarrow[C_2H_5OH]{C_2H_5ONa} \underset{\text{II}}{CH_3SNa} \xrightarrow{ClCH_2CH_2OH} \underset{\text{III}}{CH_3S{-}CH_2CH_2OH} \xrightarrow{SOCl_2}$$

$$\underset{\text{IV}}{CH_3S{-}CH_2CH_2Cl} \xrightarrow[CH_2(CO_2C_2H_5)_2]{NaOC_2H_5} \underset{\text{V}}{CH_3{-}S{-}CH_2CH_2{-}CH(CO_2C_2H_5)_2} \xrightarrow[\text{then acid}]{KOH}$$

$$\underset{\text{VI}}{CH_3{-}S{-}CH_2CH_2CH(CO_2H)_2} \xrightarrow{Br_2} \underset{\text{VII}}{CH_3SCH_2{-}CH_2\underset{Br}{C}{-}(CO_2H)_2} \xrightarrow{NH_3}$$

$$\underset{\text{VIII}}{CH_3S{-}CH_2CH_2\underset{NH_2}{C}{-}(CO_2H)_2} \longrightarrow \underset{\text{IX}}{CH_3S{-}CH_2CH_2{-}\overset{H}{\underset{NH_2}{C}}{-}CO_2H}$$

The preparation of methylthiolethyl chloride (IV) has recently been described by Kirner.[3] It was found more convenient to work with absolute alcohol solutions of sodium methyl mercaptide than to use the ether suspension which Kirner recommended, even though the yields of methylthiolethyl alcohol (III) were somewhat lower when alcohol was used as the solvent. The malonic ester reaction gave a 45% yield. The saponification of the ester and isolation of the dibasic acid ran smoothly and the yields were about 72–73% of the theoretical amount. The dibasic acid was brominated in dry ether and immediately treated with ammonia to reduce to a minimum the chance for addition of the bromo compound to the sulfur atom of the same or another molecule to give complex sulfonium salts. No intermediate products were isolated between the methylthiolethylmalonic acid (VI) and the final methionine (IX). The yield of methionine based on this malonic acid derivative was about 24%.

The product which was obtained agreed in its properties with those reported by Barger and Coyne[2] for their synthetic product.

Experimental Part

Methylthiolethyl Chloride.—Methyl isothiourea sulfate was prepared in 90–95% yield by the method of Arndt.[4] This was hydrolyzed by aqueous alkali[4] and the methyl mercaptan was absorbed in alcoholic sodium ethylate solution. The methyl mercaptan obtained by the hydrolysis of 1120 g. of methyl isothiourea sulfate was absorbed in a solution of 138 g. of sodium in 3 liters of absolute alcohol. The solution was heated to boiling and 524 g. of ethylene chlorohydrin was added from a separatory funnel at such a rate that the solution continued to reflux gently. The mixture was boiled overnight after the ethylene chlorohydrin had been added. Most of the alcohol was distilled and the concentrated solution was centrifuged to remove the sodium chloride. The salt was washed with alcohol and the washings were combined. The alcohol was removed and the methylthiolethyl alcohol was distilled under reduced pressure. The yield was about 221 g. (40% of the theoretical amount) of a product which boiled at 58–68° at 15 mm.

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[3] Kirner, THIS JOURNAL, 50, 2446 (1928).

[4] Arndt, *Ber.*, 54, 2236 (1921).

The alcohol was converted to the chloride by the method described by Kirner[3] in yields of about 60% of the theoretical amount.

Diethyl β-Methylthiolethylmalonate (V).—In a 2-liter three-necked flask fitted with a separatory funnel, a reflux condenser and a mechanical stirrer was placed 600 cc. of absolute alcohol (dried over magnesium methylate) and 30 g. of sodium was added in portions. To the slightly cooled solution of sodium ethylate was added 185 g. of diethyl malonate. Then 145 g. of methylthiolethyl chloride was added from the separatory funnel over a period of three hours. The mixture was boiled under a reflux condenser overnight to complete the reaction. The reaction mixture was then worked up in the usual manner and the malonic ester derivative was distilled under reduced pressure. The yield was 136 g. (45% of the theoretical amount) of a product which boiled at 166–167° at 30 mm. At atmospheric pressure (745 mm.) the product boiled at 275–280°; d_4^{20} 1.051; n_D^{20} 1.4675; M_D, calcd., 59.67; found, 60 57.

Anal. Subs., 0.2012, 0.1656, 0.2028: $BaSO_4$, 0.2064, 0.1680, 0.2003. Calcd. for $C_{10}H_{18}O_4S$: S, 13.67. Found: S, 14.08, 13.98, 13.97.

β-Methylthiolethylmalonic Acid (VI).—Twenty grams of the above ester were added dropwise to a boiling solution of 20 g. of potassium hydroxide in 80 cc. of 90% alcohol. The mixture was boiled under a reflux condenser for three hours. Then 100 cc. of water was added and the alcohol was distilled as completely as possible. The solution was cooled to 0° and made acid to Congo paper by the careful addition of hydrochloric acid. The water solution was extracted with ether several times. The ether layers were evaporated under reduced pressure and the residue dried in a desiccator over phosphorus pentoxide. The dried product was then purified by dissolving it in hot chloroform and adding sufficient petroleum ether to make the solution slightly turbid. On cooling the malonic acid crystallized. It was filtered and dried. There was thus obtained 11 g. (73% of the theoretical amount) of a product which melted at 92–93". The product began to lose carbon dioxide at about 128°. Titration gave a neutral equivalent of 87 instead of the theoretical 89.

Methionine (IX).—In a three-necked 300-cc. flask fitted with a reflux condenser, a separatory funnel and a mechanical stirrer, was placed a solution of 10 g. of β-methylthiolethylmalonic acid in 100 cc. of anhydrous ether. The stirrer was started and a solution of 9 g. of bromine in 50 cc. of anhydrous ether was added dropwise. The bromination started immediately and proceeded rapidly so that the color of free bromine had disappeared within a few minutes after the last of the solution had been added.

As soon as the bromine color had disappeared, the solution was poured into ten times the theoretical amount of aqueous ammonia in a glass-stoppered bottle. The mixture became warm and was cooled in ice. The mixture was shaken thoroughly to extract all of the bromo acid from the ether layer and was then allowed to stand at ordinary temperature overnight. Longer standing did not improve the yields. The ether layer was separated and discarded as it contained no valuable product. The aqueous solution was evaporated on a steam cone under reduced pressure to a volume of about 50 cc. in order to remove most of the ammonia. The residue was neutralized with a very slight excess of hydrobromic acid and evaporated to dryness. Excess hydrobromic acid had to be avoided as it seemed to destroy the methionine. When no hydrobromic acid was added a very poor yield was obtained.

The residue, which consisted of ammonium bromide and the hydrobromide of the aminomalonic acid derivative, was heated in an oil-bath held at 140" for about three hours. The residue was taken up in water and filtered to remove a little insoluble material. To the solution was added 5 cc. of pyridine and three volumes of hot alcohol. On cooling the methionine separated as white crystals. It was recrystallized by dissolving in water and precipitating with alcohol. By working over the mother liquors there was obtained a total of 2 g. (24% of the theoretical amount) of the desired amino acid. The product melted at 272° (uncorr.) and the picrolonate darkened at 176–179° and melted at 179–180°. Barger and Coyne report the two melting points as 281° and 178°, respectively.

Anal. Subs., 0.1584, 0.1080: $BaSO_4$, 0.2521, 0.1692. Calcd. for $C_5H_{11}O_2NS$ S, 21.5. Found: S, 21.84, 21.51.

Summary

A new synthesis of methionine, γ-methylthiol-α-amino-n-butyric acid, has been described.

URBANA, ILLINOIS

COMMUNICATIONS TO THE EDITOR

THE SPECTROSCOPIC DETERMINATION OF THE DECOMPOSITION PRODUCTS OF ORGANIC COMPOUNDS. BENZENE IN THE ELECTRODELESS DISCHARGE

Sir:

An interesting and beautiful phenomenon is observed if benzene vapor at about 0.1-mm. pressure is subjected to the electrodeless discharge. At first a greenish glow appears near the walls of the flask adjacent to the wires. Almost immediately this spreads through the entire flask, turns red, and is extinguished by the resultant decomposition and recombination to form a solid hydrocarbon. This stops the discharge by lowering the pressure. After 40 discharges of this type the walls of the flask are found to be covered by a thin, transparent, amber-colored deposit.

However, if benzene vapor is admitted at just the rate to keep the pressure at a value suitable for the discharge, the glow persists and the accompanying decomposition and synthesis proceed continuously for an hour or more. Thus several thousand liters of the vapor are completely decomposed and quantitatively converted into a reddish-brown flaky powder. This has the same composition as benzene, according to the analysis of Dr. I. E. Muskat, but a much higher molecular weight. The formula is thus (CH),.

The spectrum, (Fig. 1) indicates that the benzene molecules rapidly decompose into molecules of C_2 and CH, and atoms of C^+ and H. Thus the 5 groups of Swan bands, and a considerable number of the other C_2 bands, as discovered by Deslandres and D'Azambuja, were found, as well as the λ4300 and λ3900 bands of CH. In addition the first four lines of the Balmer series of hydrogen, and the line spectrum of C^+ appeared.

The C_2, CH, C^+ and H seem to combine completely to form the reddish-brown hydrocarbon, as evidenced by the fact that several thousand liters of benzene vapor decompose without giving enough gaseous residue to raise the pressure sufficiently to extinguish the discharge.

The spectra were photographed by Hilger quartz spectrographs, and a

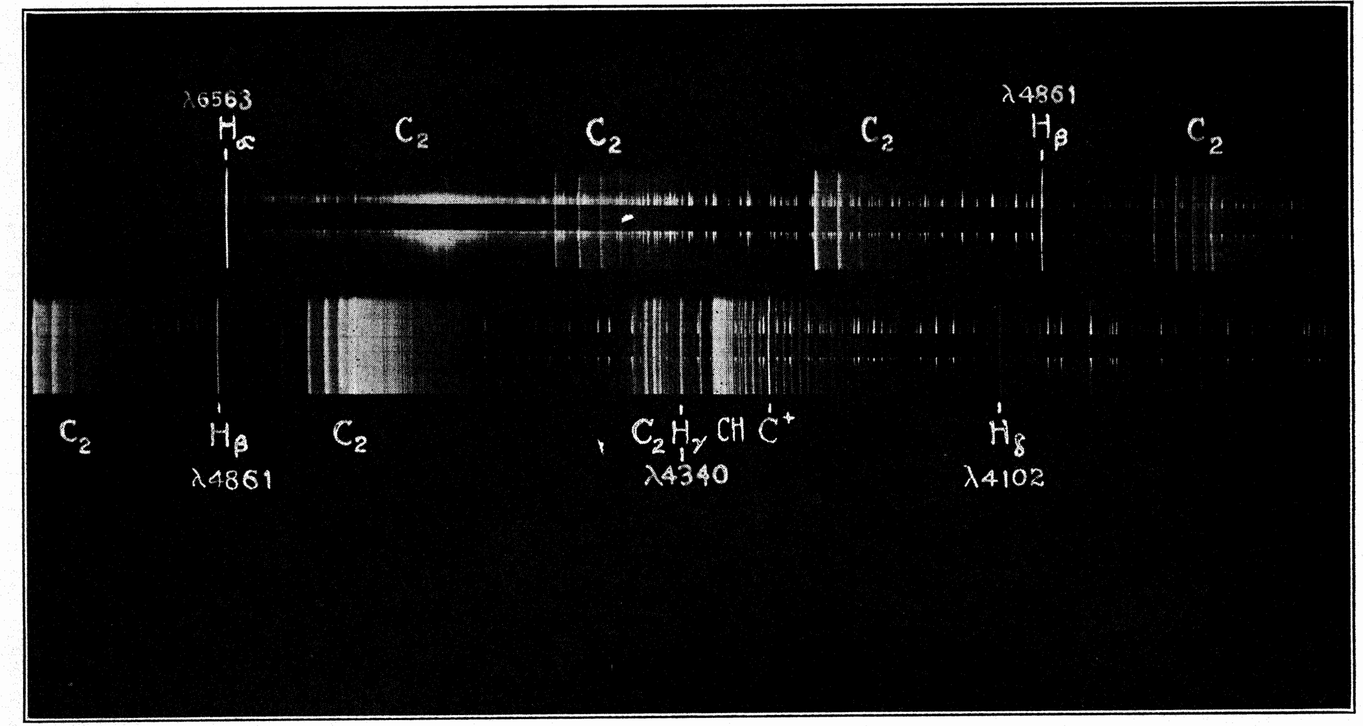

Fig. 1.—Spectrum of molecules of C_2 and CH, with the first four lines of the Balmer spectrum of hydrogen, together with lines of the C^+ spectrum, as obtained from the decomposition products of benzene in the electrodeless discharge, with a frequency of 1000 kilocycles per second.

Steinheil glass spectrograph of high dispersion. The apparatus (Fig. 2) consisted of a liter flask with a quartz window, connected with a gage and vacuum pump, and surrounded by 6 coils of wire from a 25,000-volt transformer and a condenser of 0.02 microfarads capacity. This stores about 1 calorie of energy at 25,000 volts. The benzene is dried with great care before it is put into the apparatus, and its vapor passes through a tube (D) of phosphorus pentoxide just before it enters the flask.

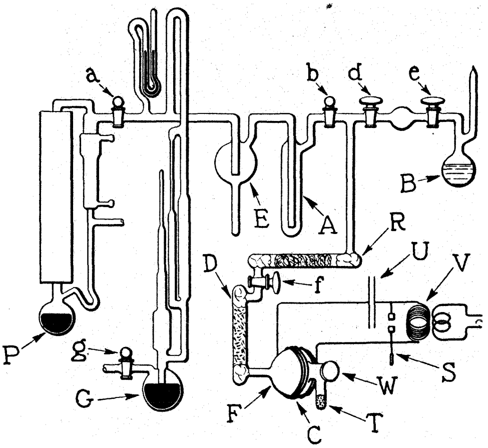

Fig. 2.—Apparatus for the decomposition of organic vapors.

The frequency of the discharge was 1000 kilocycles per second. The pressure at which the discharge acts rises with increasing distance between the terminals of the spark gap. Thus with a 1.5-mm. spark gap the maximum pressure is 0.05 mm., while with a gap of 6 mm. the maximum pressure is 0.25 mm.

In so far as the spectra found are excited by electronic collisions, the velocities of the electrons range between 1.9 and 3.6 volts or between 0.85×10^8 and 1.14×10^8 cm. per second. The limits probably extend farther in each direction. The intermediate products in the decomposition of other organic compounds, such as methane, acetylene, phenol, etc., will be determined, since the spectroscopic method is one of great convenience and usefulness.

GEORGE HERBERT JONES LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

WILLIAM D. HARKINS
DAVID M. GANS

RECEIVED MAY 2, 1930
PUBLISHED JUNE 6, 1930

THE HEAT OF FORMATION OF MOLECULAR OXYGEN

Sir:

The reported values for the heat of formation of molecular oxygen range from 162,000 to 110,000 calories. These values have all been determined by indirect methods. A direct determination of the heat of formation of molecular oxygen has now been obtained using an apparatus essentially the same as that of Bichowsky and the author[1] for hydrogen. This apparatus employs the method of Weide and Bichowsky[2] for determining the

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[1] Bichowsky and Copeland, THIS JOURNAL, 50, 1315 (1928).

[2] Weide and Bichowsky, *ibid.*, 48, 2529 (1928).

percentage dissociation of a diatomic gas. Atomic oxygen was produced by means of the electrodeless discharge. The recombination took place on the surface of a calorimeter coated with palladium black. It has been shown that water vapor is necessary for the production or at least for the maintenance of the atomic gas.

In the preliminary experiments reported at this time 16 to 25% dissociation was realized at a distance of 10 cm. from the discharge bulb at pressures of 0.1 to 0.2 mm. of mercury. The validity of the application of Knudsen's formula for the measurement of the percentage dissociation at these pressures has been established experimentally by measuring the rate of flow of oxygen through the orifices at the two limiting pressures and also the rate of flow of hydrogen at one pressure lying between these limits. The heat of formation of molecular oxygen as given by these experiments is 7.2 (± 0.2) volts or 165,000 (±5000) calories per gram molecular weight. It is to be noted that although this value is in good agreement with some of the older values, it is considerably higher than those reported within the last year. As it is quite possible that the presence of metastable atoms is giving too high a value, further experiments are now in progress using different pressures and different lengths of path, under which conditions the average life of a metastable atom should be changed. It is hoped in this manner either to prove the absence of metastable states or at least to be able to correct for their excess energy should they be present.

JEFFERSON PHYSICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
L. C. COPELAND[3]

RECEIVED MAY 3, 1930
PUBLISHED JUNE 6, 1930

ELECTRO-DEPOSITION OF METALLIC BERYLLIUM

Sir:

We wish to announce that as a result of work carried on for a number of years we have been able to obtain metallic beryllium by the electrolysis of solutions of beryllium salts in various organic and inorganic non-aqueous solvents. Although the solutions of beryllium salts in substituted ammonia give deposits of metal, the most satisfactory solvent is liquid ammonia itself either alone or with the addition of salts or other compounds which lower the vapor tension of the solution and increase the solubility of beryllium salts. Thus the metal has been prepared from solutions which may be electrolyzed at room temperature. The metal obtained by these electrolyses is so pure that it is insoluble in even the strongest acids unless the metal is in contact with a more electro-negative metal such as platinum. Under the microscope the metal is seen to be crystalline.

Hitherto all attempts to dehydrate beryllium salts have yielded basic

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[3] National Research Fellow in Chemistry.

salts, due to partial hydrolysis. We have discovered that beryllium salts may be dehydrated by heating in fused ammonium salts. Beryllium salts so dehydrated may be electrolyzed in liquid ammonia solution without removing the excess ammonium salts and yield metallic beryllium.

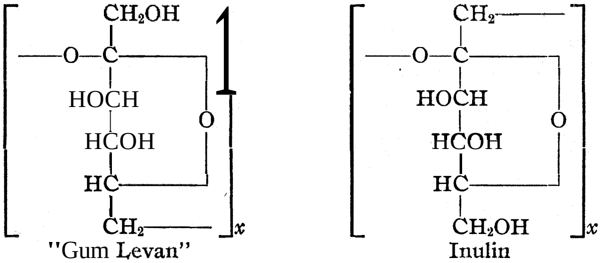
THE MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO
HAROLD SIMMONS BOOTH
G. G. TORREY

RECEIVED MAY 16, 1930
PUBLISHED JUNE 6, 1930

THE STRUCTURE OF "GUM LEVAN"

Sir:

"Gum Levan," formed by the action of *Bacillus mesentericus* on cane sugar, has been definitely identified by hydrolysis, acetylation and methylation experiments conducted in this Laboratory as a polymerized anhydrofructofuranose, the linkages being at positions 2 and 6 of the fructose sugar chain, as compared with the 1,2-linkage in the case of inulin. It can be prepared in a pure state, free from nitrogen and ash, by the action of the enzyme isolated from the organism.



"Gum Levan" Inulin

When submitted to the action of *Bacillus xylinum* it yields a new product, apparently more highly polymerized, which is at present under investigation.

Methylation of "levan" yields a trimethyl derivative which on hydrolysis gives a new crystalline 1,3,4-trimethylfructofuranose, m. p. 63°, the first crystalline γ-sugar to be isolated. Its constitution is confirmed by its inability to form an osazone, transformation to tetramethyl-γ-fructose, and oxidation by nitric acid to yield a dibasic dimethyl lactol acid. The diethyl ester of the latter on methylation and treatment with dry ammonia gives a crystalline diamide, m. p. 138°.

The bearing of these facts on the nature of plant synthesis is to be discussed in a forthcoming article.

Further researches in connection with the action of *Leuconostoc mesenteroides* and other bacteria (as well as their corresponding enzymes) on carbohydrates are in progress.

PULP AND PAPER RESEARCH INSTITUTE
MCGILL UNIVERSITY
MONTREAL, CANADA
HAROLD HIBBERT
R. STUART TIPSON

RECEIVED MAY 16, 1930
PUBLISHED JUNE 6, 1930

PHENYL URETHAN ANESTHETICS

Sir:

In a recent paper[1] the writer described several phenyl urethan derivatives of dialkyl amino alcohols, and called attention to their great local anesthetic activity. While other compounds of these amino alcohols have not been reported, the activity of the phenyl urethans immediately suggested a study of similar compounds derived from the amino alcohols which are the bases of the popular local anesthetics butyn and novocaine. These compounds were accordingly prepared by the action of phenyl isocyanate on the proper amino alcohol in ether solution. The hydrochlorides were precipitated with gaseous hydrogen chloride and recrystallized from a mixture of acetone and ethyl acetate. The γ-di-*n*-butylaminopropanol phenyl urethan hydrochloride (I) melts at 123–124° (Calcd. for $C_{18}H_{31}O_2N_2Cl$: Cl, 10.4. Found: Cl, 10.1, 10.5), and the β-diethylaminoethanol phenyl urethan hydrochloride (II) melts at 138–139° (Calcd. for $C_{13}H_{21}O_2N_2Cl$: Cl, 13.0. Found: Cl, 12.9). One per cent. aqueous solutions of butyn and novocaine and the corresponding molecular concentrations of the two homologous phenyl urethan hydrochlorides were applied to the cornea of the rabbit for one minute and the durations of the resulting anesthesias were timed. The results are as follows.

Compound	Percentage concentration	Duration of anesthesia of rabbit's cornea, minutes
Butyn	1	25
I	0.96	36
Novocaine	1	Incomplete
II	1	9

Thus both phenyl urethan derivatives produce anesthesias of decidedly longer duration than similar molecular concentrations of their *p*-aminobenzoate homologs. This material although not yet complete demonstrates most convincingly the value of a study of phenyl carbamic acid esters as local anesthetics. A further study is being made of other properties of these compounds and of the general field of phenyl urethan local anesthetics.

LABORATORY OF PHARMACOLOGY AND TOXICOLOGY
YALE UNIVERSITY SCHOOL OF MEDICINE
NEW HAVEN, CONNECTICUT

T. H. RIDER

RECEIVED MAY 17, 1930
PUBLISHED JUNE 6, 1930

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[1] Rider, THIS JOURNAL, 52, 2115 (1930).

THE PHOTOCHEMICAL DECOMPOSITION OF NO_2

Sir:

The band spectrum[1] of NO_2 shows regions of diffuse absorption below 3700 Å. and 2448 Å. These have been interpreted by R. Mecke[2] and V. Henri[3] as predissociation spectra. At 3700 Å. the NO_2 should decompose into NO and a normal O atom, whereas at 2448 Å. the oxygen atom should be in a ('D) state. If these statements are correct, then it should be possible to prove chemically the presence of oxygen atoms. Therefore mixtures of NO_2 with H_2, $H_2 + O_2$ and $CO + O_2$ have been exposed to light of various wave lengths.

With light of wave length below 3700 Å., H_2O and CO_2 were formed. From the ratio of the quanta of light absorbed to the amount of water formed it was calculated that the reaction

$$O + H_2 \longrightarrow OH + H$$

proceeds at least 10^4 times as slowly as the reaction

$$O + NO_2 \longrightarrow NO + O_2$$

when the oxygen atom is not excited. With shorter wave lengths (from Cd, Al and Zn sparks) the efficiency of water formation was greater.

From this it may be concluded that in the regions of predissociation oxygen atoms are actually produced. Furthermore, the results obtained confirm the observations of Kistiakowsky,[4] that the probability of a reaction of an O atom with H_2 forming OH + H is small. The experiments with added hydrogen and with added hydrogen and oxygen showed that at room temperature for each hydrogen atom less than two molecules of water are formed.

The details will be given in a paper soon to appear.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
HANS-JOACHIM SCHUMACHER[5]

RECEIVED MAY 19, 1930
PUBLISHED JUNE 6, 1930

THE ADSORPTION OF COMPLEX AMMONIUM IONS BY SILICA GEL

Sir:

In preparing metallized silica gels by the method of Latshaw and Reyerson,[1] it was early found that complex ammonium salts of platinum and palladium were most easily reduced to the metallic condition by adsorbed hydrogen. On the other hand, the ions of nickel and copper do not reduce

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[1] L. Harris, *Proc. Nat. Acad. Sci.*, 14, 690 (1928).

[2] R. Mecke, *Die Naturw.*, December 20 (1929); *Z. physik. Chem.*, *7B*, 108 (1930).

[3] V. Henri, *Nature*, **125**, 202 (1930).

[4] G. B. Kistiakowsky, THIS JOURNAL, **52**, 1868 (1930).

[5] International Research Fellow in Chemistry.

[1] Latshaw and Reyerson, THIS JOURNAL, 47, 610 (1925).

satisfactorily by the above method. It was, therefore, decided to attempt the reduction of complex salts of copper and nickel by passing hydrogen over silica gel containing these salts. When solutions containing complex cupric ammonium ions were poured on silica gel a surprising result occurred. The complex ammonium ions were found to be very strongly adsorbed by the silica gel. The first liquid which came through the silica gel was almost completely decolorized by the silica gel. The same result was found when complex ammonium ions of nickel were used. When these adsorbed ions are reduced by passing hydrogen over the dried gel an excellent metallic deposit results. The deposit resembles the palladium deposit of the previous method very much. We are continuing the investigation with regard to the specific adsorption of complex ions as well as the use of the metallized gels thus produced.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA
GRANT W. SMITH
L. H. REYERSON

RECEIVED MAY 26, 1930
PUBLISHED JUNE 6, 1930

NEW BOOKS

Experimental Physical Chemistry. By FARRINGTON DANIELS, J. HOWARD MATHEWS and JOHN WARREN WILLIAMS. McGraw-Hill Book Company, Inc., New York, 1929. xvi + **475 pp.** 132 figs. **14.5 X 21 cm. Price,** $3.50.

The authors state in their preface that the purposes of this book are "to illustrate the principles of physical chemistry, to train in careful experimentation, to develop familiarity with apparatus, to encourage ability in research." These purposes have led them to divide the material into three sections: Laboratory Experiments (Part I, 285 pp.), Apparatus (Part II, 145 pp.), Miscellaneous Operations (Part III, 29 pp.).

Part I provides a laboratory manual of physical chemistry which is unique both in the number and variety of exercises listed and in the treatment of the individual experiment. One might hope to cover about a third of the 78 experiments in the usual one-year laboratory course. Harassed instructors who want their laboratory outlines ready-'made will get little comfort from this book, but others will find its wide scope a convenience where equipment is limited, and a powerful stimulus to the ambitious student. If necessary or desirable, a course of 25 or more exercises may be selected, involving only the conventional types of experiments and simple forms of apparatus. On the other hand, the material is sufficiently extensive to meet the needs of an advanced course such as electrochemistry, or a course introductory to research. Some of the topics covered which are seldom if ever included elsewhere are: viscosity of gases, specific heats of liquids, partial molal volumes, conductance in mixed solvents, decomposition potentials and overvoltage, the manganese hydroxide electrode, activity and salt effect, application of the electron tube to electrometric titration, adequate experiments in colloid chemistry, excellent experiments in reaction velocity, including the decomposition of nitrogen pentoxide in carbon tetrachloride solution, electrochemistry of gases, phase-rule study of a 3-component system, photochemistry, radioactivity, including radioactive indicators, and a particularly detailed treatment of dielectric phenomena. In view of this profusion of material, some may regret the absence of experiments on gas–solid equilibria, oil films and the thermal conductivity of gases.

Each experiment is treated under the headings: Theory, Apparatus, Procedure, Calculations, Practical Applications, Suggestions for Further Work, References. "The imperative is not used. Procedures are described but orders are not given. The student must study the experiment first and then set his own pace—a method which develops both his power and his interest." In the majority of cases the theoretical treatment is adequate, even for experiments which must occasionally be performed before the material has been studied in class. The procedures as described will keep the instructor busy, but the able student is given a chance to show his mettle.

Part II briefly describes the apparatus which has been found most suitable for advanced work or research on the topics covered by Part I. While not intended as a substitute for Ostwald–Luther, this section will impress the reader with its concise and critical description of satisfactory technique and apparatus, and with its numerous and well-selected references to the original literature.

Part III consists of short chapters on Calibration, Thermostats, Thermometers, Glass Blowing and the Purification of Materials. An appendix gives tables for corrections to barometer readings, vapor pressure and density of water, and four-place logarithms. A useful subject index is included.

Only a negligible number of errors or loose expressions have been detected. For example, exception may be taken to "the D line of hydrogen" (p. 38), to the occasional loose use of "concentration" (p. 67), to the statement that "from a knowledge of the degree of ionization and concentration of the solute, it is possible to predict the electrical conductance" (p. 143), to the statement that the principle of the ordinary flowmeter is "that of the Pitot tube" (p. 293), etc. On the whole, however, the text gives evidence of unusually careful preparation.

In the reviewer's opinion this book deserves the serious consideration of every teacher of physical chemistry. It is a volume from which the capable student may obtain enough, but not too much, guidance and real inspiration, both during his course and afterward.

ARTHUR F. BENTON

Conférences d'Actualités Scientifiques et Industrielles, 1929. (Lectures on Scientific and Industrial Actualities.) Preface by J. LEMOINE. Hermann et Cie., Paris, 1930. viii + 270 pp. 126 figs. Price, paper cover, 35 francs.

This collection is a series of popular lectures delivered during the spring of 1929 under the auspices of the Conservatoire National des Arts et Metiers. The subjects and authors are: The Recent Crisis in Undulatory Optics, L. de Broglie; The Magnetic Properties of Mesomorphic Substances, G. Foex; Atoms of Light and Quanta, E. Bloch; The Photo-Electric Cell and Its Applications, L. Dunoyer; Radiation from Incandescent Objects, G. Ribaud; Electrical Production of Sound, Jullien; Structure of Spectra and of Atoms, L. Bloch; High Pressure Vapors (applied to heat engines), V. Kammerer; Directed (radio) Waves and Their Applications, R. Mesny. In all cases the treatments are non-mathematical. Naturally, therefore, the laboratory and technical applications are treated in greater detail than the theoretical issues involved. For the most part the discussions are such as to be easily grasped by one unfamiliar with the methods of advanced physics. As such they form an interesting résumé of recent developments in the respective fields.

HUGH M. SMALLWOOD

L'Atomistica Moderna e la Chimica. (Modern Atomistics and Chemistry.) BY DR. M. HAISSINSKY, with a preface by NICOLA PARRAVANO. Ulrico Hoepli, Milan, 1930. xii + 315 pp. 45 figs., 16 × 23.5 cm. Price, 35 lire.

This book, written by a young Russian chemist who studied in Rome, is intended to show how much the newer development of atomic physics can do for the chemist in explaining his results.

The first two chapters give a general and from necessity a rather sketchy review of the atomic constitution of matter, the kinetic theory of gases, the elementary charge, X-rays, radioactivity and the periodic system, the laws of thermodynamics and Nernst's theorem, with the necessity of introducing quanta.

The third chapter explains the Bohr theory of the atom and its consequences for radiation and the periodic table.

The next five chapters deal with the nature of the chemical forces from Bohr's standpoint and the connection between structure and properties, mainly for polar compounds. The author starts with Kossel's theory, the formation of complexes, dissociation, then describes the theories of Lewis and Langmuir—which are taken up again later—and then goes over to the case in which the purely electrostatic treatment has been most successful, namely, Bohr's theory of salt crystals. Chapter VII is devoted to the researches, due to a large extent to Grimm, which systematize the physico-chemical properties of inorganic compounds and connect them with the electron structure of their parts.

The eighth chapter, on the deformation of electron orbits, forms a transition to homeopolar compounds. It starts with the polarizability of atoms, proceeds then to the influence of this property on the forces of attraction in solids and solutions, on crystal structure and color and ends up with a discussion of metals and pseudo-atoms (Goldschmidt and Grimm).

The next three chapters treat reaction velocities, namely, in turn, photochemistry and its connection with absorption spectra, including the dissociation of molecules by light, then the role played by radiation in general in supplying the heat of activation, finally the connection between adsorption and catalysis. In this chapter the theory of intermediate compounds and the theory of active surface patches are explained.

The last chapter (XII) introduces the new quantum mechanics, giving first the general ideas. Then the author shows in detail, that this theory gives the real clue to the nature of the homeopolar valence bond and that the results agree very well with the older theory of Lewis and Langmuir. The new theory of metallic conduction concludes the book.

The author shows a real enthusiasm about his subject, is very clear in the presentation and shows excellent judgment in the difficult question how much deduction should be given in such a book. The first chapters contain a few errors (e. g., that in Bohr's atom the *kinetic* energy is higher farther out (p. 49)), but on the whole the book is very good. A few misprints occur (e. g., Figs. 14 and 15 should be interchanged).

KARL F. HERZFELD

Atoms, Molecules and Quanta. BY ARTHUR EDWARD RUARK, Ph.D., Physicist, Mellon Institute of Industrial Research, Lecturer in Physics at the University of Pittsburgh, and HAROLD CLAYTON UREY, Associate Professor of Chemistry at Columbia University. McGraw-Hill Book Co., Inc., 370 Seventh Avenue, New York, 1930. xvii + 790 pp. 230 figs. Price, $7.00.

The enormous volume of work which has appeared in the last few years on atomic physics has made the writing of text and reference books particularly laborious and thankless. On the other hand it has increased the necessity for such summaries. The present volume will go a long way toward filling this very real need in that it presents a coherent and detailed account of both the experimental and theoretical sides of the subject.

The authors state that their book was written to fulfil the requirements of both the newcomer to the subject and the experienced worker in the field. Regarded as a textbook the work possesses a number of advantages over its predecessors. In the first place, it is, of course, more up-to-date than the previous works. Aside from this, the authors are to be commended for having written in a style readily comprehensible to the reader who has not been trained in advanced physics. Too many of the previous books on atomic structure have been written exclusively for the physicist, leaving the chemist, among others, to puzzle over an unfamiliar vocabulary and mode of presentation. This fault has been obviated in the earlier parts of the book and minimized in the more advanced portions.

The approach to the subject is made by a detailed description of the classical experiments which led to the formulation of the older quantum theories. The authors then give a concise review of theoretical mechanics. This chapter will be of particular value to the student. The treatment is amplified by a number of illustrative examples worked out in detail, but it is regrettable that the authors have not seen fit to include a number of workable problems. The development continues with a complete account of atomic and molecular spectra and the allied topics. Detailed discussions of the periodic system and of collision processes are also included in the review of the experimental work. Throughout this part of the book the Bohr model of the atom is to a large extent retained. This is a procedure which may be open to criticism, but on the whole the authors have made their point to the effect that this retention of the older picture, in opposition to the trend of recent work toward elimination of too concrete models, is justifiable in a textbook in view of the greater clarity attained. Wherever the conclusions of the older theory have been altered by the new, the fact is pointed out and reference to the later treatment is given. The last two hundred pages of the book are devoted to a description of the quantum mechanics of Schrodinger, Heisenberg and others. The treatment is clear and the material well arranged, but it is with this section that the student will probably experience the greatest difficulty, due for the most part to the slowness of becoming conversant with the mathematical vernacular.

Taken as a textbook the work should be a valuable addition to the student's library, from which he may expect to obtain the ability to read current papers on the subject with intelligence and to apply the material both to his immediate work and to the formulation of new problems.

Regarded as a reference, the volume cannot be expected to be as valuable as it may be as a textbook. This is due to the fact that the large number of topics considered has necessitated a brevity of treatment which seems inconsistent with the function of a work of reference. Even so, a book of this size cannot be justly criticized for the omission or compression of particular topics. One wonders, however, why the subject of radioactivity has been condensed to a scant four pages and why no mention is made of the recent theoretical treatment of this topic.

On the whole, however, the authors are to be congratulated on having made a distinctive addition to the literature of the new physics; an addition which, it may confidently be hoped, will be a source of inspiration to all those who approach this latest field of conquest.

HUGH M. SMALLWOOD

Kristallzeichnen. (Crystal Drawing.) By DR. ROBERT L. PARKER, Lecturer at the Technical High School of Zurich. Gebrüder Borntraeger, W 35 Schoneberger Ufer 12 a, Berlin, Germany, 1929. vi + 112 pp. 35 figs. 24 X 23.5 cm. Price, M. 30.

Chemists have shown increasing interest in the problems of crystallography and crystal structure. This is one of the few books devoted entirely to the subject of crystal drawing and should prove very useful to those interested in the subject. It does not claim to be an exhaustive treatise.

The book is divided into two parts. The first part deals with the theory and practice of crystal drawing methods. Formulas are derived and methods of drawing are presented by figures. After a discussion of orthographic and clinographic projections, the methods of intersection of edges on an axial cross, of coordinates of direction points of intersections on an axial cross, of stereographic projection and of gnomonic projection, are described.

The author presents in detail a new method using the directions of intersection edges. The directions of these edges are calculated in terms of azimuth angles from [001] taken as 0°.

Tables, used to determine azimuth angles of various intersection edges for isometric crystals and twenty common, non-isometric minerais, are given in the second part of the book. A moderate supply of drawing sheets accompanies the book for use with the tables in drawing.

This book should be in every chemical library where crystal problems are being studied.

J. F. SCHAIRER

Jahrbuch der organischen Chemie. (Yearbook of Organic Chemistry.) By Professor Dr. JULIUS SCHMIDT, Stuttgart. Franz Deuticke, Leipzig, Germany, and Vienna, Austria, 1930. xvi + 249 pp. 17.5 X 25.5 cm. Price, unbound, M. 24; bound, M. 27.

In fulfilment of the promise made in the preceding number, the fourteenth volume of the Jahrbuch, dealing with the investigations completed in 1927, has appeared within half a year. The general plan and scope are the same as heretofore. The contents reflect the increasing interest of organic chemists in natural products but the author also devotes considerable space to papers that deal with subjects of more general interest—the stereochemistry of nitrogen compounds and of bicyclic ring systems, the metallic derivatives of the aliphatic hydrocarbons, polynuclear hydrocarbons with condensed ring systems, and the like.

E. P. KOHLER

A Brief Introduction to the Use of Beilstein's "Handbuch der organischen Chemie." By ERNEST HAMLIN HUNTRESS, Ph.D., Assistant Professor of Organic Chemistry, Massachusetts Institute of Technology. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1930. viii + 35 pp. 15 X 23 cm. Price, $1.00.

Beilstein, the "organic chemists' Bible," is too widely known to warrant description. There are, however, exceptional cases. One such was a foreign student who after having our beginners' course at Iowa State College went to Michigan to complete his undergraduate work. Incidental to some orienting questions, Professor Gomberg asked him if he knew "Beilstein." The reply was "No, he does not teach at Amcs."

Refreshing as such ignorance may be, it is as nothing compared with a beginner's facile use of the fourth edition of Beilstein now appearing as occasional volumes. In November, 1926, Dr. Stelzner informed us that there were then approximately 240,000 organic compounds, and the annual growth was about 6000. There will be then in June, 1930, about 261,000 organic compounds. This is, of course, a rough approximation, but it gives one a fair idea of the increasing importance of the correct use of the system of classification to be followed in the continuous flow of new Beilsteins. Particularly is this the case when one reflects that "complete indexes" will only be available at about 10-year intervals.

"The magnitude of the classification is such that some explanation of the main plan is desirable before the significance of its details can be appreciated. The main purpose of the pamphlet is to present the fundamentals of the scheme of classification in such a form that its students can obtain a sort of aerial view of the plan before proceeding with its details. For this reason, many interesting and intrinsically important phases have necessarily been omitted or restricted in scope of treatment." Dr. Huntress' pamphlet admirably achieves its objective. There are many who will want to read it before turning to the guide for the use of Beilstein which was published last year by The German Chemical Society. Some may despair at the thought that the system is such that we now have, in a manner of speaking, an elementary guide to the use of a complete guide for the ready use of Beilstein. Whether we like it or not, and we may rejoice in it in time, there is a system for all compounds to come and the mastery of this system is essential for the proper use of Beilstein.

HENRY GILMAN

Die Methoden der organischen Chemie. Ein Handbuch für die Arbeiten im Laboratorium. Vol. III. (Methods of Organic Chemistry. A Handbook for Laboratory Work.) Third, fully revised and enlarged edition. Edited by Professor Dr. J. HOUBEN, Berlin. Verlag Georg Thieme, Antonstrasse 15/19, Leipzig C 1, Germany, 1930. xxxviii + 1451 pp. 41 figs. Price, unbound, M 166; bound, M. 176.

Few new editions can be so certain of a cordial reception from organic chemists as Houben's "Methods of Organic Chemistry." Refinements of technique, new applications of physico-chemical methods to problems in organic chemistry, and new methods of detection, analysis and synthesis are usually dispersed in such a mass of current literature that only the most patient search discloses the best method available for preparing a substance or attacking a problem. Here "the Houben" brings relief because each succeeding edition has invariably reviewed the literature almost to the date of issue. The present edition of the third volume is no exception.

For those who have used the second edition it will be sufficient to know that nearly the whole of this volume was prepared by the same competent men who were responsible for the second edition. The ground covered is likewise nearly the same—the only change being the inclusion of a chapter on anthocyanins in place of the section on polymerization which has already appeared in the third edition of the second volume. The great increase in size, therefore, is due to the incorporation of the new material which has accumulated in the decade between the two editions.

For those who are unfamiliar with the earlier edition it may be useful to point out that the title of this text very inadequately describes its contents. This is in reality a very extensive treatise on organic chemistry written not merely—or even primarily—for those who need to know something about organic compounds, but for all those who have occasion to work with them, and the separate sections have been prepared by collaborators who have worked with distinction in the subjects which they present. It comes from, and it is intended for the workshop, but its authors have not been content with merely providing directions for mechanical experimentation. A summary of a chapter taken at random from one of the shorter sections will serve to illustrate the treatment.

The chapter on oxido compounds was prepared by Meerwein, who is familiar with the field because he has made a systematic investigation of the action of benzo peracid on unsaturated hydrocarbons. It begins with a brief discussion of the classification and nomenclature of oxido compounds, then proceeds to a description of seven methods of preparation including the most recent methods for obtaining oxido ketones and glycidic esters. The description is accompanied by a discussion which gives a knowledge of the facts necessary for an intelligent choice, the reactions involved, numerous illustrations and an excellent bibliography. The methods of preparation are followed by a section dealing with the detection, properties and transformations of oxido compounds. This includes intramolecular rearrangements as well as the numerous addition reactions and like the section on preparation is accompanied by discussion, illustration and bibliography. No systematic text on organic chemistry contains such an adequate account of the chemistry of oxido compounds, and here as well as in many other sections it is a distinct advantage to have open-chained and cyclic representatives treated in the same place.

The volume contains an excellent author and subject index and its typography and arrangement are admirable. Evidently such a treatise should not only be accessible in chemical libraries, but should also be on the tables of organic investigators to whom it is indispensable. The reviewer regrets, therefore, that with increase in size, its price has mounted until it is almost beyond the reach of the individual.

E. P. KOHLER

The Chemistry of the Colloidal State. A Textbook for an Introductory Course. BY JOHN C. WARE, Sc.M., Ph.D., Associate Professor of Chemistry, New York University (Washington Square College Division). John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1930. xiv + 313 pp. 96 figs. 15.5 × 23.5 cm. Price, 83.75.

This book containing fourteen chapters has been written for the beginner in colloid chemistry. The author has treated the subject in a non-mathematical style. The text appears to be written for students having a meager training in physical chemistry.

There is lacking in the text the continuity which the reviewer had hoped for. The chapter on Interfacial Phenomena (non-electrical) is followed not by a chapter on Interfacial Phenomena (electrical) but by one on Turbidity in Colloidal Suspensions. A whole chapter is devoted to Turbidity, Nephelometry and Colorimetry. Another chapter is devoted to Silica Gel and its Use in Adsorption. The three hundred pages are rounded out with a concluding chapter on Catalysis by Contact Agents.

The reviewer is disappointed not so much with the treatment of the subject matter which is presented as with the selection and arrangement of that included. The beginner in the field of colloid chemistry will find much of interest in this text. The numerous references to the literature will stimulate his desire for further reading.

A. L. ELDER

Ultraviolet **Light** and Vitamin D in Nutrition. By KATHARINE BLUNT, President of Connecticut College, and RUTH COWAN, Instructor in Home Economics, The University of Chicago. The University of Chicago Press, Chicago, Illinois, 1930. xiii + 229 pp. 39 figs. 14.5 × 21.5 cm. Price, $2.50.

This interesting book of 229 pages is a very well written summary of the work of the last few years in the study of the effects of ultraviolet light and vitamin D. Inasmuch as the discovery of vitamin D is really less than ten years old, it is remarkable how much work has been accomplished by these studies. In fact, it has been extremely difficult to keep up with the literature in this field. Miss Blunt and Miss Cowan have summarized the enormous amount of work and done it in an extremely interesting way. They have recorded the literature in sufficient detail and then, at the end of each chapter, have summarized the results. The book, therefore, is very interesting reading as well as an excellent source of information. To anyone who is interested in the field this book is an excellent beginning for further studies. It has summarized in a very fair way all the literature up to 1929.

JOSEPH C. AUB

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[FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE MANGANOUS–MANGANESE DIOXIDE AND THE MANGANOUS–PERMANGANATE ELECTRODES

BY DENTON J. BROWN AND HERMAN A. LIEBHAFSKY

RECEIVED JUNE 29, 1928 PUBLISHED JULY 3, 1930

The following investigation was undertaken in order to secure a more accurate "normal potential" for the manganous–manganese dioxide electrode. It constitutes the final step necessary for the calculation of the oxidation potential of the manganous–permanganate electrode.

I. The Manganous–Manganese Dioxide Electrode.—The data in the literature for this electrode are very discordant. The value for the normal potential usually given is based on the consistent results of Tower.[1] Smith[2] in an attempt to use this electrode for the determination of the concentration of the hydrogen ion, failed to duplicate the observations made by Tower. In both cases the manganese dioxide was deposited electrolytically. Brown and Tefft[3] failed to prepare pure manganese dioxide, or manganese dioxide hydrated, or with water only as a contamination, by electrolysis.

Preliminary observations made in this Laboratory indicated that the more consistent results obtained by Tower were due to a very exact duplication of conditions in the depositions of the manganese dioxide. The determinations proved that the manganese dioxide deposited electrolytically was apparently in a more active state than that prepared by the method used by Brown and Tefft.[3] The electrodes prepared by depositing manganese dioxide electrolytically were in a more active form and as *a* result the data of Tower could not be used to calculate the true equilibrium values.

The electromotive force of the cell $H_2/HClO_4(m_1)$, $Mn(ClO_4)_2(m_2)/MnO_2$, in which *m* indicates the molality, was studied at 25°. The equation to represent the reaction of the cell is $MnO_2 + 2HClO_4 + H_2 \longrightarrow Mn(ClO_4)_2 + 2H_2O$ and to represent the manganous–manganese dioxide electrode (as observed), $MnO_2 + 4H^+ + 2e \longrightarrow Mn^{++} + 2H_2O$.

The "normal potential," E_0, of the manganous–manganese dioxide

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[1] Tower, *Z. physik. Chem.*, 18, 17 (1895).

[2] Smith, *ibid.*, 21, 93 (1896).

[3] Brown and Tefft, THIS JOURNAL, 48,1128 (1926).

electrode can be calculated from the electromotive force, E_c, which is the observed value corrected to 76 cm. for hydrogen, and the activities, a, of the hydrogen ion and manganous ion at the given concentrations, by using the equation $E_0 = E_c - 0.05915/2 \log a_{H^+}^2/a_{Mn^{++}}$.

This equation requires the activity coefficients for manganous salts and of perchloric acid when they are in solution with each other. To eliminate the use of these doubtful values, an attempt was made to make all observations on solutions in which the manganous perchlorate and the perchloric acid were of equal molality (Table I). The value E' may be calculated from the equation

$$E' = E_c - 0.05915/2 \log m_1^2/m_2 = E_c - 0.05915/2 \log m$$

and E_0 may be determined by extrapolating the values for E' to zero molality if observations can be made at high dilution. It was discovered that at greater dilutions than 0.05 molal a dark deposit appeared on the hydrogen electrode and caused fluctuations in the observed values large enough to introduce considerable error in the plotting of the curve. However, the mean of these inaccurate values was near the curve extrapolated to 1.235 volts.

In order to meet the difficulty a second series (Table II) of measurements was made in which the perchloric acid was kept at tenth molal while the concentration of the manganous perchlorate was varied. The standard potential E_0 was calculated on the assumption that the activity coefficient for the manganous perchlorate followed the values given by Lewis and Randall[4] for similar salts and that the $Mn(ClO_4)_2$ in the experimental electrode could be considered as $2HClO_4$ for the purpose of determining a, the activity. Of course, for the more dilute solution this correction becomes practically zero and is a very small correction for the two more concentrated solutions.

Experimental Part

Manganese dioxide was prepared by slowly decomposing at 150°, the best manganous nitrate obtainable, treating the residue at that temperature four times with nitric acid, pulverizing, washing several times with conductivity water and finally heating at 250–300° for four hours. Analysis of the dioxide thus prepared showed it to be at least 99.9% pure. Water was the only detectable impurity.

The wash water from the manganese dioxide was tested for manganese; since none was found we assumed all to be changed to dioxide. There was a slight reduction of a dilute permanganate solution due to oxides of nitrogen. The washed dioxide was heated to 250–300° and tested as given above; the results were negative. By analysis this final product contained 100 ± 0.1% of manganese dioxide. To determine the possible presence of

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[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 362.

oxides of nitrogen, we heated a considerable portion to a high temperature; a slight deposit of moisture was all that was observed. Our observations indicate that the manganese dioxide has a great adsorptive capacity for water and oxides of nitrogen. Heating directly to 250–300° did not remove the latter.

Manganous perchlorate was prepared by the action of perchloric acid on the best grade of manganous carbonate. The strength of this solution was determined by decomposing a weighed sample by the method given above and weighing the manganese dioxide.

In all cases efforts were made to have chemicals specially purified. Conductivity water was used to prepare all solutions.

The powdered manganese dioxide and the electrode solution were rotated at 25° for three hours before they were placed in the electrode vessel.

The half cell consisted simply of a test-tube with a sealed on side arm to serve as a liquid connection to the hydrogen electrode, and a one-holed stopper through which was inserted a glass tube with a platinum foil sealed in it at the lower end and filled with mercury to make contact. The platinum foil is always completely immersed in the solution.

Since the same solution appears throughout the cell, the hydrogen electrode was separated from the manganese dioxide electrode only by a stopcock to prevent possible diffusion of hydrogen. This was opened only while measuring.

The potentials were measured at 25° with a Leeds and Northrup Type K potentiometer, an L and N Type 2500 galvanometer, and a new standard cell calibrated by the Bureau of Standards was employed to check the reference cell.

The cells prepared as described above show no radical fluctuations; some of them were observed for a month and no change greater than two millivolts was observed. The cells were usually measured over a period of a few days before the final reading was taken. If the solution was not rotated with the manganese dioxide, a steady change of the electromotive force took place for a period of days. The initial value was low by about 0.1 volt, rose to a maximum usually several millivolts above the final equilibrium values, and then decreased to constant value.

TABLE I

EXPERIMENTAL RESULTS

m $HClO_4$ and *m* $Mn(ClO_4)_2$	E_c, mv.	E
0.3	1.2402 ± 0.8	1.2557
.2	1.2336 ± 0.3	1.2543
.1	1.2202 ± 0.5	1.2498
.05	1.2054 ± 0.3	1.2439

By extrapolating the curve for E, the value 1.235 is obtained.

TABLE II

EXPERIMENTAL RESULTS

m HClO$_4$	m Mn(ClO$_4$)$_2$	E_c, mv.	Eo
0.0940	0.050	1.2360 ± 0.1	1.238
.0992	.010	1.2525 ± 0.6	1.238
.0978	.005	1.2580 ± 0.4	1.237
.0983	.002	1.2663 ± 0.4	1.236
.0983	.001	1.2726 ± 0.4	1.234
		Average	1.237

Based on these results the value +1.236 for the normal potential of the electrode $MnO_2 + 4H^+ + 2e \quad Mn^{++} + 2H_2O$ is probably correct within 2 mv.

II. The Manganous-Permanganate Electrode.—Using the value +1.586 determined by Brown and Tefft[3] for the potential of the manganese dioxide-permanganate electrode and the value as determined above, the calculated value for the manganous-permanganate electrode in the presence of an acid at unit activity is +1.446 volts.

Summary

A value of +1.236 volts was obtained for the oxidation potential of the reaction $MnO_2 + 4H^+ + 2e \quad Mn^{++} + 2H_2O$ in perchloric acid solution.

For the oxidation potential of the reaction $MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{++} + 4H_2O$, the value +1.446 volts was calculated.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

CHLORIDE-FREE FERRIC OXIDE HYDROSOLS AND THE BURTON-BISHOP RULE

BY R. C. JUDD AND C. H. SORUM

RECEIVED AUGUST 12, 1929 PUBLISHED JULY 3, 1930

Introduction

Although the general validity of the Burton-Bishop rule[1] relative to the effect of concentration of colloid on the flocculation values of electrolytes seems to be quite well established in the case of the widely studied arsenic trisulfide sols, it is quite as definitely discredited by the behavior of ferric oxide hydrosols. Kruyt and van der Spek[2] have shown that for colloidal hydrous ferric oxide the precipitation values of all electrolytes, monovalent as well as di- and trivalent, decrease with dilution of

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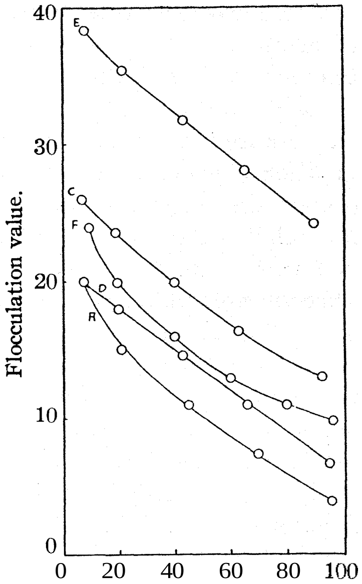
[1] Burton and Bishop, *J. Phys. Chem.*, *24*, 701 (1920).

[2] Kruyt and van der Spek, *Z. Kolloidchemie*, 25, 3 (1919).

the sol. These results have been further verified by Weiser and Nicholas[3] and Boutaric and Perrean.[4]

Inasmuch as the ferric oxide hydrosols prepared in this Laboratory[5] seem to be different from ferric oxide sols previously investigated, it was deemed important to study the influence of change of concentration of sol upon the flocculation values of electrolytes with this particular colloid.

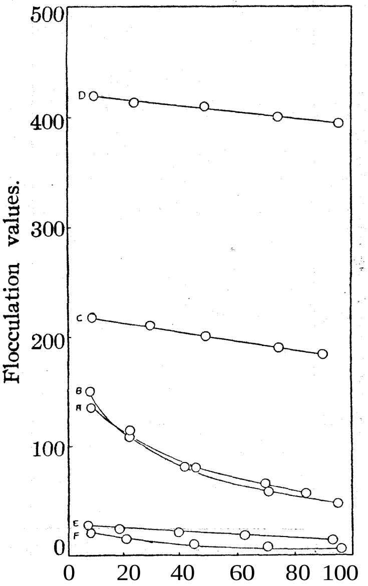
Preparation and Purification of Sol.—The chloride-free sol was prepared and purified in accordance with the method already described.[5] In its final purified state it contained 3.042 g. of iron per liter.



Percentage sol concentration.

A, NaCl; C, KCl; D, $KBrO_3$; E, $K_4Fe(CN)_6$; F, NaCl.

Fig. 1.—Variation of flocculation values of monovalent ions with sol concentration.



Percentage sol concentration.

A, $NaNO_3$; B, $AgNO_3$; C, $Al(NO_3)_3$; D, $ThCl_4$; E, KCl; F, NaCl.

Fig. 2.—Variation of flocculation values of monovalent anions accompanied by cations of different valences.

Coagulation Studies.—The classical method of adding electrolyte directly to the sol and noting the concentration required to cause complete coagulation after a given length of time, being the method upon which the previously mentioned conclusions were based, was employed. The details of this method were as follows. Exact volumes of sol placed in pyrex test-tubes were diluted to ten cubic centimeters with solutions of electro-

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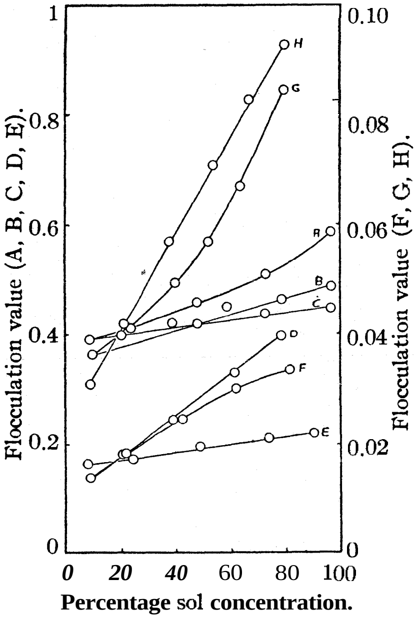
[3] Weiser and Nicholas, J. *Phys. Chem.*, *25*, *742* (1921).

[4] Boutaric and Perrean, J. *chim. phys.*, *24*, 496 (1927).

[5] Sorum, THIS JOURNAL, 50, 1263 (1928).

lyte of varying concentrations. The minimum final electrolyte concentration required to cause complete clearing after two hours was taken as the flocculation value. The flocculation value is recorded as millimoles of electrolyte per liter of final solution. The original undiluted sol, containing **3.042** g. of iron per liter, was taken as the 100% sol. The different percentage dilutions were calculated on the basis of the final volume of the flocculation mixture.

The results of the flocculation studies are summarized graphically in Figs. 1, 2 and 3. They emphasize the fact that the ferric oxide sol studied followed the rule of Burton and Bishop.



A, K_2SO_4; B, $K_2C_2O_4$; C, Na_2SO_4; D, $K_2Cr_2O_7$; E, Ag_2SO_4; F, $K_4Fe(CN)_6$; G, $K_3Fe(CN)_6$; H, $NaKC_4H_4O_6$.

Fig. 3.—Variation of flocculation values of polyvalent anions accompanied by monovalent cations.

Reference to Fig. 2 will show that the concentration of monovalent anion required to cause complete flocculation depends to a marked degree upon the valence of the cation with which it is associated; the higher the valence of the cation the greater the flocculation value of the given anion. This is in agreement with Weiser's conclusions.[6]

A comparison of these flocculation values with those reported by other investigators working with the same electrolytes and similar ferric oxide sols[7] will show that the latter are uniformly higher.

The behavior of potassium ferrocyanide as shown in Curves 3F and 1E is typically irregular. In 3F the sol is positive and shows flocculation values consistent with its behavior toward a high-valence negative ion. Higher concentrations of ferrocyanide have reversed it to a negative sol in 1E, where its behavior is typical of that of a negative sol toward a monovalent positive ion.

The Influence of Ferric Chloride on Flocculation Values of Sodium Chloride.—In reviewing the results of the study up to this point, it is to be noted that the sol under observation has three features which seem to distinguish it from other ferric oxide sols. First, it contains no detect-

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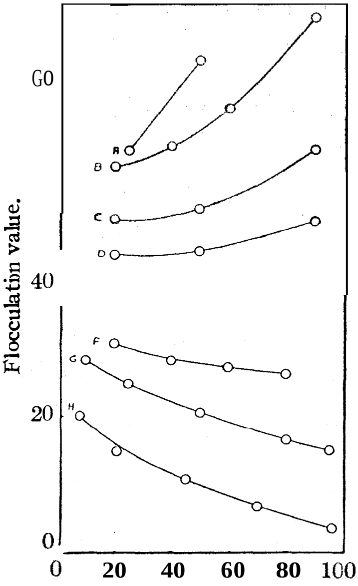
[6] **Weiser, "Colloid Symposium Monograph," 1926, Vol. IV, p. 354.**

[7] **Kruyt and van der Spek, *Kolloid-Z.*, 25, 1 (1919).**

able chloride ion; second, it requires uniformly lower concentrations of electrolyte to cause coagulation; third, it follows the Burton–Bishop rule. The immediate inference would be that the first feature, that is, freedom from chloride, is responsible for the second and third. To test this inference, ferric chloride was added in varying amounts to the pure sol and the flocculation values for sodium chloride obtained as before. The results are summarized in Fig. 4.



Percentage sol concentration.

Millimoles of $FeCl_3$ added per liter: A, Kruyt's values; B, 0.16; C, 0.12; D, 0.10; E, 0.09; F, 0.06; G, 0.03; H, 0.00.

Fig. 4.—Influence of $FeCl_3$ on variation of flocculation values of sodium chloride.

They indicate very definitely that flocculation values and flocculation behavior are a function of the purity of the sol. They suggest that the failure of ferric oxide sols to follow the Burton–Bishop rule is due to lack of purity of the sol. They seem to justify the claim that the ferric oxide sols prepared in this Laboratory are more pure, more nearly free from electrolyte, than the ferric oxide sols that have been studied elsewhere. These pure sols obey the Burton–Bishop rule; also, they give lower flocculation values. On being treated with ferric chloride they cease to obey the above rule, and the flocculation values immediately become higher. Apparently, they obey the Burton–Bishop rule and have low flocculation values because the amount of impurity present is quite low.

As previously noted the sol contained 3.042 g. of iron per liter. This corresponds to 4.34 g., or 27.125 millimoles of iron oxide per liter. By consulting Curve B, Fig. 4, it will be noted that when 0.16 millimole of ferric chloride per liter was added, both the actual flocculation value for sodium chloride and the relation of flocculation value and sol concentration come very close to the values given by Kruyt,[7] (Curve A, Fig. 4). The ratio of the number of millimoles of ferric oxide to millimoles of ferric chloride added is 169.5. This ratio comes reasonably close to the values claimed by investigators who have made a study of the chloride content of carefully purified sols.[8]

Summary

1. A chloride-free ferric oxide hydrosol was prepared by high-temperature hydrolysis and dialysis of ferric chloride.

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[8] Pauli and Rogan, *Kolloid-Z.*, 35, 131, 1924.

2. Flocculation values for a number of electrolytes were determined by the classical method.

3. The chloride-free ferric oxide sol prepared was found to differ from ferric oxide sols prepared and studied by other investigators in that it followed the Burton–Bishop coagulation rule. Furthermore, it gave uniformly lower flocculation values than did these sols. By adding chloride to this chloride-free sol its behavior could be made to conform to that displayed by similar sols prepared by other investigators. The conclusion was drawn that the striking behavior of this sol was due to the absence of detectable chloride. This behavior serves to emphasize the fact that the variation of the flocculation value of anions with dilution of the sol is a function of the purity of the sol; that is, the validity or invalidity of the Burton–Bishop rule is apparently determined by the purity of the sol.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

THE SOLUBILITY, SPECIFIC GRAVITY AND INDEX OF REFRACTION OF AQUEOUS SOLUTIONS OF FUMARIC, MALEIC AND *i*-MALIC ACIDS

BY N. A. LANGE AND M. H. SINKS

RECEIVED OCTOBER 25, 1929 PUBLISHED JULY 3, 1930

The stereoisomerism of these acids makes any data on them of theoretical interest. The physical properties are scattered throughout the literature, mostly as isolated observations; the latest and most comprehensive list of values are those reported by Weiss and Downs.[1] The present investigation was undertaken with a view of obtaining a more complete series of values—the solubility in water at rather close intervals of temperature, the density of aqueous solutions and the refractive index of aqueous solutions. The values for the solubility are in good agreement with those reported by Weiss and Downs with the exception of the solubility of maleic acid at 60°; the value at this temperature as reported by them was found to be very close to the solubility at 50°.

The acids used in these determinations were the commercial grades which were subjected to a further purification. After two crystallizations from water it was found that the melting points of maleic and fumaric acids remained constant. Malic acid, which is very soluble in water, was purified by a crystallization from water, filtering, digesting the crystals with hot acetone, cooling to room temperature, filtering and air drying at room temperature. The three acids were then dried in *vacuo* at room temperature; the melting points of maleic, fumaric and malic acids thus obtained were found to be 130, 284 and 128.5°, respectively. Weighed samples when dis-

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[1] J. M. Weiss and C. R. Downs, THIS JOURNAL, 45, 1003 (1923).

solved in water and titrated against standard 0.1 *N* sodium hydroxide solution (standardized against pure succinic acid) showed a purity of +99.8%. All of the data obtained in this work are based upon weights in air.

Solubility in Water.—The solubility determinations were made by suspending an excess of the acid in water contained in 100-cc. Soxhlet flasks which were then almost completely immersed in a water-bath which was maintained at the desired temperature within ±0.2°. The temperature was determined by means of thermometers which had recently been calibrated by the U. S. Bureau of Standards. The contents of the flask was kept agitated by means of a glass stirrer. Samples of the solution were taken from the flask by means of a small pipet of about 5–6-cc. capacity (the low solubility of fumaric acid necessitated using larger pipets) which had previously been brought to the temperature of the solution under investigation. After removal of the cotton filter from the tip of the pipet, the weight of the sample in the pipet was determined, the sample transferred to a beaker for titration or to a volumetric flask for titration against standard 0.1 N sodium hydroxide solution with phenolphthalein indicator. The solubility equilibrium was approached from both temperature directions. Several successive samples were taken at each temperature to determine when equilibrium was attained and it was found that 12 to 14 hours of agitation was sufficient. Determinations were made at approximately 5° intervals of temperature and from these results a curve was plotted. The following equations express the solubility (C) of the acids in water at temperatures (t) between 5 and 80° in terms of grams of acid per 100 g. of solution. The solubility for maleic acid is nearly a straight line and the two equations for this acid as given below give values within the limits of experimental error.

Fumaric acid $\log C = 0.016721 - 0.6362$

i-Malic acid $C = 0.438t + 47.04$

Maleic acid $C = 0.6455 + 28.2$ (for temperatures from 5 to 40°), and

$C = 0.492t + 34.5$ (for temperatures above 40°)

Specific Gravity of Aqueous Solutions.—The densities of the solutions at 20/4° were determined by dissolving the acid in water, filtering, diluting to different extents and determining the specific gravity of the various dilutions by means of a pycnometer; the concentration of acid in each of the various dilutions was determined by titration of weighed samples of solution against standard 0.1 N sodium hydroxide with phenolphthalein indicator. From these results a curve was plotted. The curves were exceedingly regular and that in the case of maleic acid was a straight line; the curve for *i*-malic acid is nearly a straight line, for which the following two equations of straight lines give values within the limits of experimental error. No values for the specific gravity of fumaric acid solutions are given because of the low solubility of this acid at 20°. The following equations express the concentration (C) of acid in grams per 100 g. of aqueous solution corresponding to the specific gravity (d) at 20° referred to water at 4°.

Maleic acid $C = 276.78(d - 0.9982)$, for values of d up to 1.071
i-Malic acid $C = 244.55\ (d - 0.9982)$, for values of d less than 1.108, and
$C = 216.17(d - 0.9839)$ for values of d from 1.108 to 1.169

Index of Refraction.—The index of refraction was determined at 20° on aqueous solutions prepared as described under specific gravity and the readings were made with a Zeiss immersion refractometer using the prism which gives a reading of 14.5 with distilled water at 20° ($14.5 = n_D = 1.33301$). The following equations express the concentration of acid in grams per 100 g. of aqueous solution corresponding to the immersion refractometer reading (r).

Fumaric acid g./100 g. of solution $= 0.263r - 3.814$ (for values of r from 14.5 to 16.3)
Maleic acid g./100 g. of solution $= 0.272r - 3.922$ (for values of r from 14.5 to 95)
Malic acid g./100 g. of solution $= 0.323r - 4.68$ (for values of r from 14.5 to 45.5), and
g./100 g. of solution $= 0.289r - 3.132$ (for values of r from 45.5 to 95)

Summary

The solubility, specific gravity and index of refraction of aqueous solutions of fumaric, maleic and i-malic acids have been determined; equations representing these values are given.

CLEVELAND, OHIO

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE VELOCITY OF SAPONIFICATION OF ETHYL FORMATE BY AMMONIUM HYDROXIDE IN THE PRESENCE OF AMMONIUM SALTS

BY EDWARD NOEL ROBERTS AND ETHEL M. TERRY

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In early work by Drs. Julius Stieglitz and Edith E. Barnard[1] of this Laboratory, it was found that although ethyl and methyl formates are hydrolyzed at immense speed in dilute solutions of strong bases,[2] the velocity of these reactions may be measured in suitable mixtures of ammonium hydroxide and ammonium salts. The present paper[3] represents a continuation of this work in the case of ethyl formate.

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[1] The work referred to had been completed before 1911.

[2] Bibliography of published reports on the alkaline hydrolysis of methyl and ethyl formates: (a) Trautz and Volkmann, *Z. physik. Chem.*, **64**, 53 (1908); (b) Nernst, Ber., 42, 3178 (1909); (c) Handa, *ibid.*, **42**, 3179 (1909); (d) Eucken, *Z. physik. Chem.*, **71**, 550 (1910); (e) Skrabal and Sperk, *Monatsh.*, 38, 191 (1917). Only the last reference contains data bearing on the present problem. Reference will be made to this later.

[3] The experimental work of this paper was completed in 1918 by Dr. Roberts in partial fulfilment of the requirements for the degree of Doctor of Philosophy at this University. See also Terry and Stieglitz, THIS JOURNAL, **49**, 2216 (1927).

The solutions were always near to 0.08 normal (formula weight per liter of solution) with respect to ester and near to 0.1 normal with respect to ammonium hydroxide. The normality of the salt present at the start of the reaction varied from 0.04 to 0.4. The salts used were ammonium chloride, ammonium nitrate and ammonium formate. The reactions were carried out at 25°.

Experimental Detail

Mixtures of aqueous solutions of ammonium salt, ammonium hydroxide and ethyl formate were made in the container of a special apparatus, described elsewhere,[4] which was designed to permit the rapid removal of accurately measured samples of the mixture for analysis. These samples, which were of volumes close to 99 cc., were discharged at noted times into measured quantities of standard hydrochloric acid which had been kept at 0°. The mixture was then partly frozen and in the course of an hour the excess of acid was determined by titration, care being taken to see that the last of the ice had melted before the titration was completed. The apparatus in which the main reaction occurred was contained in a de Khotinsky thermostat the temperature of which was constant to ±0.01°. The temperature of the reaction mixture was always within 0.15° of that of the bath throughout the major portion of the time during which samples were taken.[5] It was found by experiment that under these conditions the temperature of the reaction mixture could be read by means of a Beckmann thermometer mounted with its bulb in that solution.

As mercury was employed in the special apparatus for displacement of samples of the reaction mixture, it was necessary to be sure that mercury had no effect on the basicity of the mixture. Therefore, solutions containing mixtures of ammonium hydroxide, ammonium chloride and sodium formate were exposed to the action of mercury under conditions to be used in the measurements. No losses of basic strength were found.

The discharge of samples into hydrochloric acid at 0° stopped the reaction provided the quantity of acid used was only slightly in excess of that required to neutralize the ammonium hydroxide present. It will be remembered that Manning[6] has found that the coefficient of autocatalysis of ethyl formate is 4.8 moles per minute per unit concentration of hydrogen ion at 25°. From this it will be appreciated that it was necessary to keep the hydrogen-ion concentration small during the time the neutralized samples were stored. Under the conditions used, samples could be kept for two hours. It was our practice to complete the titrations within an hour of the time the samples were withdrawn.

The titrations were completed using ammonium hydroxide as base and azolitmin as indicator. In order to find the correct color for the end-point, sample solutions of ammonium formate were made from standardized ammonium hydroxide and formic acid solutions and to these sufficient ammonium chloride or nitrate was added to duplicate the composition of samples to be taken from the reaction mixtures. It developed that the same color could be used in all cases[7] provided the titration were carried out at 0°.

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[4] Gooch and Terry, THIS JOURNAL, 51,1959 (1929).

[5] Owing to an oversight this condition of experiment was not mentioned in the earlier papers, see Refs. 3, 4 and 8. It has been faithfully maintained in all our work. [E. M. T.]

[6] Manning, *J. Chem. Soc.*, 119,2079 (1921).

[7] Kolthoff, *Rec. trav. chim.*, 41, 54 (1922), has demonstrated that the color of azolitmin in solutions of P_H equal to 7.0–7.1 in a phosphate buffered solution represents a

A 0.15% azolitmin solution was used in the proportion of 0.055 cc. for every 10 cc. of volume of sample at the completion of the titration.

The same precautions were taken to prevent the solutions from taking up carbon dioxide that had been employed in earlier work.[8]

Three or more samples of the reaction mixture were used for the determination of the concentration of ammonia, free and combined, in the solutions. Each sample was first neutralized with hydrochloric acid, and then transferred to a suitable apparatus; concentrated sodium hydroxide was then run in and the freed ammonia distilled into a known quantity of hydrochloric acid in the well-known manner. These analyses were made on mixtures of known composition with and without the additional presence of formates in them but no difference in result was found. Therefore the method was considered satisfactory. The initial concentration of ammonium hydroxide in a given reaction was calculated from the dilution of the stock solution and the concentration of ammonium salt present was calculated from the difference in concentration of total ammonia, free and combined, and the concentration of the free base. As will be shown later these last terms serve only to show the preparation of the reaction mixture. They are not used in the calculation of the coefficient of the reaction.

The ammonium hydroxide was made by allowing gas from a tank to be absorbed in water of high purity, as shown by its conductivity. Ammonium nitrate and chloride were of C. P. grade dissolved in water and the solution filtered in contact with air free from carbon dioxide.

Freshly distilled ester was used for all solutions. Most of the material was from Kahlbaum but some was made in this Laboratory from the reaction of ethyl alcohol and formic acid catalyzed by hydrogen chloride. No difference in rate of reaction was shown by the two products.

Calculation of Results

It seemed probable that for intervals of the reaction for which the activity coefficient of the ammonium salt present might be considered constant, the activity coefficient of ionized ammonium hydroxide might likewise be constant and that under these conditions the rate of the reaction would be equal to a coefficient times the product of the respective molalities (formula weight per 1000 g. of water) of ammonium hydroxide and of ester divided by the molality of the ammonium salts present at the moment in question. Therefore, as a preliminary step, a series of reaction coefficients was calculated as shown below for the intervals in which the activity coefficient of the ammonium salt might be considered constant to 0.5%. It was assumed that the activity coefficient of the ammonium salts would be the same as that characteristic of potassium chloride at like molality, and Scatchard's values were used.[9]

Let B, E and S be the initial molalities of ammonium hydroxide, ester and

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PH of 6.6 in a 0.5 normal potassium chloride solution likewise buffered. It is doubtless this salt effect that accounts for the fact that the same color could be used for all end-points in spite of the fact that with increasing ammonium salt content of the solution the apparent basicity of ammonium hydroxide decreased so that the PH of the correct end-point decreased. However, the validity of our use of the indicator does not rest on Kolthoff's observation but on experimental tests.

[8] Wilson and Terry, THIS JOURNAL, 50, 1250 (1928).

[9] Scatchard, *ibid.*, 47, 654 (1925).

salt, respectively; let X be the molality of ester or base which has been transformed by the reaction up to the time t; let K_1 be the reaction coefficient; then at this moment t

$$dX/dt = K_1(B - X)(E - X)/(S + X) \quad (1)$$

The integrated form of this expression for the interval $t_2 - t_1$ is

$$K_1(t_2 - t_1) = [2.303/(B - E)][(E + S) \log (E - X_1)/(E - X_2) - (B + S) \log (B - X_1)/(B - X_2)] \quad (2)$$

Certain short cuts were used in the application of this equation. In place of $(E + S)$, $(B + S)$ and $(B - E)$, the same data in terms of normality were used since the factor for conversion of normality to molality would have canceled. The ratio $(B - X_1)/(B - X_2)$ was calculated as $(b - x_1)/(b - x_2)$, the ratio of the number of cc. of standard acid required to neutralize unit volume of the reaction mixture in the respective samples. The number of cc. of standard acid equivalent to the ester present in the sample was found from the difference $(b - x) - (b - e) = (e - x)$, the term $(b - e)$ being the number of cc. of standard acid used to neutralize the base in a sample taken at the end of the reaction. The ratio $(e - x_1)/(e - x_2)$ gave the value of $(E - X_1)/(E - X_2)$.

In Table I will be found details of three representative experiments. Column headings will be understood from the above. In place of $(b - x)$ and $(e - x)$, values one hundred times greater are given to avoid printing decimals.

In Table II will be found a summary of all experiments.

An average temperature per minute[10] was calculated for each experiment and the value of the coefficient corrected by 0.66% for each tenth degree difference in temperature from 25.00°. This correction is the same as that found for the hydrolysis of ethyl acetate.[11] In Expt. 1 of Table I the correction has been applied to each value of K_1, since the temperature correction was sufficiently large to make difficult the observation of the constancy of the uncorrected coefficient. In other experiments the correction was applied to the average of the coefficients, since the temperature change was relatively small.

Although the total error of volume measurements was not over 0.10 cc. per sample and the error in reading the end-point of a titration ranged

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[10] Since temperature readings were taken at noted times and at frequent intervals, the average temperature of each small interval could be considered as the mean of the two readings, taken at the beginning and at the end. The average temperature for the time (t_2-t_1) was taken as equal to the sum of the products of the average temperature of each small interval by the duration of the interval, divided by (t_2-t_1). This manner of finding the average temperature was satisfactory since the temperature readings were taken at such intervals that the change of reading was a matter of three or four hundredths at most. All the temperature readings taken are not shown in the experiments of Table I.

[11] Skrabal and Sperk, Ref. 2e, have shown that the temperature coefficient of alkaline hydrolysis of methyl and ethyl formates is close to 2, as is the case for ethyl acetate.

from 0.03 to 0.06 cc. according to the molality of salt present, the effect on the value of the coefficient was large because the calculation, as appears in Equation 2, depends on the difference of two values' which are not far apart. The difference is larger and the effect of the error smaller the greater the value of (B − *E*) and the nearer the experiment is to completion. Errors from timing are insignificant except where short time intervals were used, as for example in Expt. 1 of Table I. The net effect of all errors was never greater than 3.5% of the value of the average coefficient of each experiment.

TABLE I

DETAILS OF THREE REPRESENTATIVE MEASUREMENTS OF THE RATE OF HYDROLYSIS OF ETHYL FORMATE BY AMMONIUM HYDROXIDE IN AQUEOUS SALT SOLUTION

Part **1**. Composition of the solution at the start of the reaction in terms of normality: ester, **0.1142;** NH_4OH, **0.1358;** salt, zero. Normality of acid used in titration, **0.1003;** volume of each sample **98.05** cc.; temperature of thermostat, 25.50°.

No.	Temp., °C.	Time, minutes	$(b-x) \times 100$	$(e-x) \times 100$	Molality of salt	Data used in calcn. (Col. I)	γ_{NH_4Cl} at t_1 and t_2	$K_1 \times 100$	$K_1 \times 100$ at 25.00°
1	25.435	4.20	8193	6068	0.050				
2	25.525	6.03	7502	5377	.059				
3	25.565	7.13	7157	5032	.063	1,3	**0.807—0.790**	**4.84**	**4.68**
4	25.585	8.18	6967	4742	.066	2,4	.795— .787	**5.03**	**4.90**
5	25.605	9.30	6620	4495	.068	3,5	.790— .785	**4.96**	**4.77**
6	25.615	10.52	6368	4243	.071	4,6	.787— .782	**4.89**	**4.70**
7	25.620	11.52	6191	4066	.073	5,7	.785— .780	**4.94**	**4.74**
8	25.625	12.70	5994	3869	.075	6,8	.782— .778	**4.90**	**4.70**
9	25.625	13.82	5828	3703	.077	7,9	.780— .776	**5.01**	**4.81**
10	25.625	15.00	5659	3534	.078	8,10	.778— .775	**5.11**	**4.90**
								Average	**4.78**

Part II. Composition of the solution at the start of the reaction in terms of normality: ester, **0.0751;** NH_4OH, **0.1119;** NH_4Cl, **0.1241.** Normality of acid used in titration, **0.09765;** volume of each sample, **98.86** cc.; temperature of thermostat, 25 00°.

No.	Temp., °C.	Time, minutes	$(b-x) \times 100$	$(e-x) \times 100$	Molality of salt	Data used in calcn. (Col. I)	γ_{NH_4Cl} at t_1 and t_2	K_1
1	25.02	2.27	9924	6193	0.14			
2	25.06	3.60	9616	5885	.14			
3	25.12	9.40	8538	4807	.15	1,3	**0.740—0.735**	**0.0571**
4	25.12	10.70	8348	4617	.15	2,4	.740— .735	.0569
5	25.12	16.83	7586	3855	.16	3,5	.735— .730	.0583
6	25.11	24.97	6873	3142	.17	4,5	.735— ,730	.0586
7	25.08	26.40	6770	3039	.17	5,6	.730— .725	.0586
8	25.07	41.70	5922	2191	.18	5,7	.730— .725	.0584
9	25.06	43.17	5864	2133	.18	7,8	.725— .721	.0593
10						7,9	.725— .721	.0593
							Average	.0583
							Value at 25.00°	.0579

TABLE I (Concluded)

Part III. Composition of the solution at the start of the reaction in terms of normality: ester, 0.0787; NH_4OH, 0.1038; NH_4Cl, 0.3902. **Normality of acid used in titration,** 0.09765; **volume of each sample,** 98.83 **cc.; temperature of thermostat,** 25.00°.

No.	Temp., °C.	Time, minutes	$(b-x)$	$(e-x)$	Molality of salt	Data used in calcn. (Col I)	γ_{NH_4Cl} at t_1 and ti	K_1
1	25.02	2 33	9365	6824	0 41			
2	25.04	3.85	9186	6642	.41			
3	25 07	11.98	8338	5797	.42	1,3	0 667−0.665	0.0789
4	25.09	14 35	8134	5593	.42	2,4	.667− .665	.0779
5	25.10	22 00	7538	4997	.43	3,5	.665− .664	.0788
6	25.09	23 23	7445	4904	.43	4,6	.665− .664	.0807
7	25.07	49.03	6105	3564	.44	5,7	.664− .662	.0800
8	25.06	50.40	6053	3512	.44	6,8	.664− .662	.0796
9	25.05	90.73	4920	2379	.46	7,9	.662− .660	.0790
10	25.04	92.13	4889	2348	.46	8,10	.662− .660	.0794
							Average	.0793

Average temperature per minute, 25.08. K_1 **at** 25.00 0.789

TABLE II

SUMMARY OF EXPERIMENTS ON THE HYDROLYSIS OF ETHYL FORMATE BY AQUEOUS AMMONIUM HYDROXIDE

No.	Normality at zero time (a) ester	of (b) NH_4OH	(c) salt (NH_4Cl)	Average molality of salt	Average K_1	Average temp., °C.	K_1 at 25.00°
			Part I				
1	0.0784	0.1038	0.3912	0.430	0.0818	25.12	0.0812
2	.0787	.1038	.2902	.435	.0793	25.08	.0789
3	.0859	.1038	.3912	435	.0803	25.07	.0799
4	.0769	.1038	.3960	.435	.0825	25.29	.0809
5	.0751	.1119	,1241	16	.0583	25.10	.0579
6	.0796	.1119	.1214	.16	.0563	25.10	.0559
7	.0792	.1123	,0390	.075	.0524	25.05	.0522
8	.0758	.1123	.0838	.109	.0524	25.03	.0523
			Part II				
			(NH_4NO_3)				
1	0 0717	0.1312	0.1085	0 16	0.0559	25.07	0.0555
2	.0766	.1125	.456	50	.0825	25.06	.0823
			Part III				
1	0.1075	0.1320	0.0	0060	0.0460	24.81	0.0466
2	.1123	.1322	.0	.064	.0468	25.10	.0465
3	.1142	.1358	0	.069	.0497	25.56	.0479

Values of K_1 given in Table II will be seen to vary greatly with the molality of the salt present. Thus for 0.109 molal salt solution K_1 equals 0.054 and for 0.43 molal salt K_1 is 0.0818, an increase of 56%.

Significance of the Results

In searching for an explanation of the variations of K_1 it is obviously necessary to consider the possibility not only of catalysis by ionized ammonium hydroxide, but also of two other parallel reactions, the one, the decomposition of the ester brought about by water, and the other, an ammonia catalyzed change.[12a]

The second of these reactions may be eliminated since Manning[6] found no evidence of it in his study of the autocatalyzed hydrolysis of ethyl formate at 25° and the reactions reported on were much slower than those here considered.

For the evaluation of factors of the remaining reaction, the activity coefficients of ammonium hydroxide in ammonium salt solution are needed and these have not yet been determined. Therefore a final analysis of the significance of the results of the present work may not now be made. Since some time must elapse before either of the authors can continue work in this field, it has seemed best to put the present data on record without waiting for the missing data.

It will occur to the reader that since the solutions are dilute it is probable that for our experiments the corresponding thermodynamic data for ammonium hydroxide, 0.5 molal, in potassium chloride solutions at 25°, reported by Harned and Robinson[13] may be used as approximate activity coefficients of ammonium hydroxide in the present instance. The point of uncertainty is, of course, the possibility that ammonium ion has some specific effect on the activity of ammonia (and vice *versa).*

It may, therefore, be of interest that if equations are set up to represent the rate of the reactions as dependent on two reactions, one an hydrolysis of ester by ionized ammonium hydroxide and the other an ammonia catalyzed change, and the data of Harned and Robinson above referred to are used in evaluating the molality of ionized base and of ammonia (the ionization constant of ammonia being taken as 1.81×10^{-5}), it will be found that the coefficient of the first reaction may be taken as 1350 and that of the second reaction as 0.78 gram molecular weights per 1000 g. of water per minute.

Skrabal and Sperk[2e] estimate the coefficient of hydrolysis of ethyl formate by hydroxide ion to be 1400 gram molecular weights per liter of water per minute. Although no great weight may be attached to the close agreement of their value with the one obtained as described above, since the ionization constant of water appears as a factor in the Skrabal and Sperk calculation, it is worthy of note that the two values are of the same magnitude.

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[12] (a) Early in his work on the substituted ammonia compounds, Professor Stieglitz (see Refs. 1 and 2) foresaw the possibility that ammonia might function as a basic catalyst. Although Professor Stieglitz has published no account of his views, it seems proper to mention them here since we had the benefit of them at the time the experiments were made. More recently Professor Brönsted, Ref. 12b, has developed the same idea independently and has been the first to publish a quantitative statement of the theory. (b) Bronsted and Guggenheim, THIS JOURNAL, 49, 2554 (1927). (c) Brönsted, *Rec, trav. chim.*, 42,718 (1923); *J. Phys. Chem.*, 30,777 (1926).

[13] Harned and Robinson, THIS JOURNAL, **50,** 3157 (1928).

The ratio of 1350/0.78 or 1730/1 is within 11% of the ratio of the corresponding coefficients for the mutarotation of glucose as calculated by Brönsted and Guggenheim.[12b] (These coefficients are 6200 and 3.2 formula weights of glucose per liter per minute.) According to the Brönsted theory a fairly close agreement is to be expected, with some exceptions, between the ratio of the coefficients of catalysis by hydroxide ion and by ammonia.

Thus the results gained by using the Harned and Robinson coefficients are in harmony with expectations based on independent evidence. Since the details of the calculations follow conventional lines and since no proof can be given that the Harned and Robinson data must apply exactly, the above material is given in abstract simply as an answer to an obvious question.

Whether the assumptions made in writing Equation 1 are valid need not be argued at the present time since the coefficients calculated by means of this equation and presented in Tables I and II represent a convenient epitome of our results and that is the first purpose of this paper.

Summary

Measurements are described of the rate of the reaction of ethyl formate at 25° at molalities near 0.08 with aqueous ammonium hydroxide at molalities near 0.10 in various solutions containing either ammonium chloride, nitrate or formate. Coefficients of the rate of the reaction are reported for intervals of the reaction in which the activity coefficient of the ammonium salt may be considered constant. These coefficients have been calculated on the assumption that the rate of the reaction at any moment of time is directly proportional to the coefficient times the product of the respective molalities of base and ester and is inversely portional to the molality of salt present. The data are presented primarily to record new experiments on the reaction of an ester in ammonium hydroxide–ammonium salt solutions. Owing to the lack of thermodynamic data no final interpretation is possible at present. A tentative interpretation is given in abstract.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE X-RAY PHOTOCHEMICAL REACTION BETWEEN POTASSIUM OXALATE AND MERCURIC CHLORIDE

BY W. E. ROSEVEARE

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Many investigators have studied the photochemical reaction between mercuric chloride and oxalates as represented by the equation

$$2HgCl_2 + C_2O_4^{=} = Hg_2Cl_2 + 2Cl^- + 2CO_2$$

The results, however, have not been satisfactory due to three uncertainties, namely, the catalysis of very small traces of iron salts, the inhibition by oxygen and the formation of a white precipitate which reflects the light, making the amount of light absorbed by the solution uncertain. In the present investigation these uncertainties were eliminated.

Experimental

Apparatus.—The cylindrical reaction chamber A shown in Fig. 1 was made by fusing together the bottoms of two 250-cc. pyrex beakers. This was surrounded by a glass water jacket through which water from the thermostat was pumped. The front side was covered with a layer of cotton which provided thermal insulation yet only slightly absorbed x-rays. The length of the chamber was 6.8 cm. and the diameter 6.5 cm. The chamber was connected to the mercury manometer by a small glass capillary and a 15-cm. length of capillary rubber tubing B. The height of the mercury in the manometer was measured with the aid of a cathetometer to one-tenth of a millimeter. All measurements were made at constant volume with the mercury at the point C so that the volume of the tubing connected to the reaction chamber was relatively so small that a change of 10° in the temperature of the room would not change the pressure 0.05%. The reaction chamber was supported by a shaking mechanism which gave it short and sharp jerks, thereby shaking the solution vigorously.

The x-rays were generated by a Coolidge x-ray tube operated directly on 60-cycle alternating current with a peak voltage of 120,000. The power input was kept constant by means of ballast tubes. The tungsten target was 50 cm. from the reaction vessel and the latter was entirely exposed to the rays when the shutter E was open.

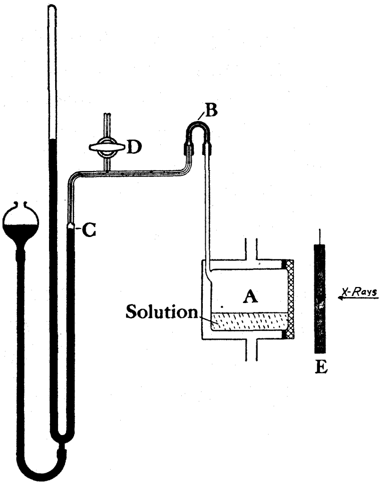

Fig. 1.

The energy of the x-rays entering the reaction chamber was determined by the calorimeter shown in Fig. 2. The center part F is a lead disk 2.50 cm. in diameter and 0.85 mm. thick which is supported in the center of a heavy iron ring G by the forty wires of the chromel–x–copel thermopile. The flattened junctions of the thermopile were attached to the disk by means of a thin layer of sealing wax which provided both thermal contact and electrical insulation. A spiral coil made from 15 cm. of No. 40

silk-covered manganin wire was imbedded in a thin layer of sealing wax on the face of the lead disk. Two No. 36 copper wires led out from the coil making thermal but not electrical contact with the heavy iron ring before passing out of the case. The resistance of the manganin coil was 20.57 ohms. The iron ring was suspended by means of silk thread in a glass case with a thin aluminum window in front of the lead disk. This case was packed in cotton to prevent air currents and radiation in the room from affecting the thermopile. A lead screen H shielded the iron ring from the x-rays.

The mercuric chloride, potassium oxalate and potassium chloride were all twice recrystallized from the c. p. quality materials. The ferric chloride used was Baker's c. p. The carbon dioxide was obtained from a cylinder and passed over fresh copper turnings at 400° to remove oxygen.

Experimental Procedure.—In all cases 50 cc. of solution was measured into the reaction chamber with a pipet. The rubber capillary tube was then slipped over the neck, fastened with wire and then coated with paraffin to prevent any leaks. In order to remove the oxygen, which inhibits the reaction, the apparatus was evacuated to within 5 mm. of the vapor pressure of water and then oxygen-free carbon dioxide admitted to atmospheric pressure. The chamber was shaken vigorously for two minutes to saturate the solution with the carbon dioxide and to shake out the oxygen into the carbon dioxide above the solution. This same process of evacuating and admitting carbon dioxide was repeated nine times. The carbon dioxide would boil vigorously out of the solution for about two minutes under the reduced pressure, carrying the oxygen out with it. Before measuring the rate, the vacuum stopcock D was closed and the apparatus shaken until the pressure no longer changed The manometer was read and then the lead x-ray shutter E was opened for a definite length of time. The chamber was again shaken until the pressure became constant and then the manometer was read.

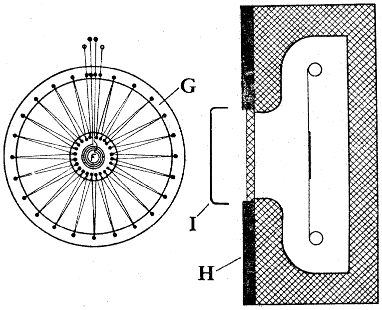

Fig. 2.

The energy of the x-rays was determined by placing the calorimeter in the exact position in which the center of the reaction chamber had been in all the experiments. The reaction chamber was broken in half and the front end placed in front of the calorimeter so that the latter would directly measure the power entering the reaction chamber in all experiments for the area of the lead disk. When the x-rays were turned on, the galvanometer connected to the thermopile gave a deflection of about 20 cm. The x-rays were shut off and a current was started through the manganin coil. This current was adjusted until the galvanometer gave the same deflection as with the x-rays. Then the power of the absorbed x-rays would be equal to I^2R where R is the resistance of the manganin coil and I the current passed through it. This current was repeatedly found to be 1.55 milliamperes.

Experimental Results

Effect of Mercuric Chloride Concentration.—The order of the reaction with respect to mercuric chloride was determined using a solution in which the amount of potassium oxalate was equivalent to more than ten times the quantity of mercuric chloride present. Under these conditions the total observed order of the reaction would be that of the mercuric chloride. The results are given in Tables I and II, respectively, with and without the ad-

Table I

25°, $HgCl_2$ 0.1164 M, $K_2C_2O_4$ 0.620 *M*, Oxygen Free

Minutes	Pressure (CO_2 + H_2O)	$(a-x)$ mole/liter	$-$Log $(a-x)$	K (1st power)
0	2.74	0.1164	0.9342	...
1	8.49	.1005	0.9977	0.0635
2	13.22	.0865	1.0632	.0655
4	20.79	.0649	1.1879	.0624
6	26.02	.0450	1.3014	.0568
11	33.69	.0281	1.551	.050
25	41.09	.0070	2.126	.043
40	43.20	.0038	2.418	.018
0	3.04	.1164	0.9342	
1.5	11.60	.0919	1.0365	.0682
2	14.12	.0848	1.0718	.0706
3	18.37	.0726	1.1389	.0671

Table II

25°, $HgCl_2$ 0.1164 M, $K_2C_2O_4$ 0.620 *M*, KCl 0.2327 M

Minutes	Pressure, cm.	$(a-x)$ mole/liter	$-$Log $(a-x)$	*K* (1st Power)
0	2.65	0.1164	0.9342	...
1	4.64	.1107	0.9558	0.0216
3	8.49	.0998	1.0011	.0225
7	14.85	.0816	1.0883	.0218
11	19.52	.0683	1.1658	.0194
16	23.84	.0559	1,2522	.0173
25	29.16	.0408	1.3897	.0153
45	35.76	.0219	1.6588	.0135

dition of potassium chloride. The rate approximates a first-order law until the reaction is near completion and then the rate rapidly falls off. Such a decrease is to be expected due to the retarding effect of the chloride ion formed by the reaction. Also, as the reaction proceeds, a larger proportion of the energy will be absorbed by the mercurous chloride precipitate and this should cause a decrease in the observed reaction rate. In order to avoid these effects, the rate was measured using a solution similar to those of Table I except that the mercuric chloride concentration was made exactly one-half as large. The rate constant in Table III, is in good agreement with that in Table I, and therefore it is evident that the rate of the reaction varies as the first power of the mercuric chloride concentration. It will also be noted that in all cases the rate constant increased during

Table III

Same as Table I except $HgCl_2$ 0.0582 *M*

Minutes	Pressure	$(a-x)$	$-$Log $(a-x)$	*K* (1st Power)
0	2.56	0.0582	1.2352	...
1.5	6.74	.0463	1.3348	0.0664
3.5	11.11	.0338	1.4713	.0687

the first part of the reaction, thus showing an induction period which is characteristic of many other chain reactions.

Effect of **Oxalate** Concentration.—The order of the reaction was determined for a solution containing equivalent amounts of oxalate and mercuric chloride. The results given in Table IV, show that the rate obeys a second-order law. Since the reaction is first order with respect to the mercuric chloride it seems evident, under these conditions, that the rate varies as the first power of the oxalate concentration. However, this is not true where the equivalent concentration of the oxalate is greater than the concentration of the mercuric chloride. The effect of the oxalate at various concentrations was determined using solutions similar in every way except having different oxalate concentrations and measuring the rate during a short interval of time during which there would only be a negligible change in the composition of the solution. These results are summarized in Table V. In the first two solutions, doubling the concentration of the oxalate almost exactly doubles the rate, but as the latter concentration is increased the effect of doubling it grows very small. Such a change in the effect of the oxalate suggests that the reaction is the decomposition of a moderately stable complex between mercuric chloride and the oxalate. The calculated values of the rate given in the table were obtained by assuming the rate equation $dx/dt = 0.575(HgCl_2C_2O_4^=)$ and the equilibrium: $(HgCl_2)(C_2O_4^=) = 0.01\ (HgCl_2C_2O_4^=)$. The agreement between the calculated and measured values of the rate, over a twenty-fold range of concentration, is strong evidence that the reaction is the decomposition of the

TABLE IV

$HgCl_2$ 0.116 *M*, $K_2C_2O_4$ 0.580 *M*

Minutes	Pressure	$(a-x)$ mole/liter	$\frac{1}{(a-x)}$	K (2nd Order)
0	2.56	0.1164	8.58	..
0.5	4.06	.1123	8.91	0.66
1	5.45	.1081	9.25	.68
2.5	9.08	.0978	10.23	.65
4	12.15	.0890	11.24	.67
7	17.31	.0742	13.46	.74
11	22.23	.0603	16.60	.78
16	26.06	.04934	20.27	.73
24	29.63	.03915	25.25	.62

TABLE V

25°, $HgCl_2$ 0.1164 M

$K_2C_2O_4$ concn.	0.0291	0.0582	0.155	0.310	0.620
Rate (meas.)	.0151	.0316	.0574	.0615	.066
Rate (calcd.)	.0151	.0290	.0568	.0638	.066
$(HgCl_2C_2O_4^=)$	.0262	.0505	.0988	.111	.114

complex $HgCl_2C_2O_4^=$. Bekhterev[1] has shown that mercuric chloride forms a complex with potassium oxalate.

Effect of Chloride Ion.—Chloride ion retards the reaction at all concentrations, but the extent varies with the concentration. This effect was investigated by measuring the rates of reaction of solutions differing only in the chloride-ion concentration. The rates were measured during short intervals of time so that there would only be a negligible change in the concentrations. The results are given in Table VI. At higher concentrations of chloride ion, doubling the concentration makes the rate one-quarter as large, so that the rate varies as the inverse second power of the chloride-ion concentration. At lower concentrations, however, the effect becomes less. This is what one would expect from the equilibria $(HgCl_2)(Cl^-) = k(HgCl_3^-)$ and $(HgCl_2)(Cl^-)^2 = k' (HgCl^=)$. When the chloride-ion concentration is large, the mercury will nearly all be present as $HgCl_4^=$ and then the concentration of the $HgCl_2$ would be inversely proportional to the second power of the chloride-ion concentration. Therefore, the rate must be proportional to the concentration of the $HgCl_2$ molecules.

TABLE VI

25°, $HgCl_2$ 0.1164 *M*, $K_2C_2O_4$ 0.620 M

KCl mole/liter	1.5616	0.9308	0.2327	0.1164	0.0000
Rate	0.00028	.00122	.0218	.0378	.066

The Effect of Oxygen.—Oxygen was found to inhibit the reaction at all observed pressures from 0.019 to 8.0 cm., a four hundred-fold range. The solutions were freed of oxygen and the given pressure of oxygen admitted, except for pressures below 0.4 cm., which were obtained by admitting known volumes of carbon dioxide containing 5% of oxygen. The rates were measured during short intervals of time during which the concentration did not change more than 2%. The results are given in Table VII. The calculated values of the rate given in the third column were obtained from the empirical equation

$$\frac{dx}{dt} = \frac{0.560}{0.0823 + (O_2)}$$

At the higher oxygen concentrations the rate is inversely proportional to the oxygen concentration, but at lower concentrations the effect of oxygen becomes less.

The Effect of Ferric Chloride.—The inhibition by ferric chloride was investigated in the same manner as the inhibition by oxygen. It was found impossible to obtain reproducible rate measurements with ferric chloride concentrations between 7×10^{-6} and $2 \times 10^{-7}M$. There is more uncertainty with the smallest iron salt concentration since under these conditions a trace of oxygen would induce an appreciable dark reaction at

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[1] Bekhterev, *J. Russ. Phys.-Chem. Soc.*, 57, 161 (1925).

TABLE VII

25°, $HgCl_2$ 0.0972 *M*, $K_2C_2O_4$ 0.898 M

Oxygen press., cm.	Rate, %/min.	Rate (calcd.)
0.0000	6.8	6.8
.0192	6.18	5.5
.0383	4.73	4.6
.075	3.46	3.56
.148	2.52	2.43
.284	1.52	1 53
.40	1.14	1.16
.55	0.87	0.89
.86	.59	.59
1.89	.274	.284
4.03	.140	.136
8.05	.075	.069

TABLE VIII

25°, $HgCl_2$ 0.0972 *M*, $K_2C_2O_4$ 0.898 M, OXYGEN FREE

$FeCl_3$, $m \times 10^3$	Rate, %/min.	Rate (calcd.)
None	6.8	6.8
	6.8	
	6.9	
0.0078	3.77	3.95
	3.82	
	3.94	
.016	2.43	2.74
.062	1.08	1.01
.25	0.333	.29
	.336	
.50	.196	.14
1.00	.091	.073
	.095	

room temperature. Some of the results given in Table VIII are given in duplicate or triplicate to show their reproducibility. The values given in the third column of Table VIII were calculated from the empirical equation

$$\frac{dx}{dt} = \frac{0.560}{0.0823 + 7630(FeCl_3)}$$

This equation differs from that for oxygen only in that the (O_2) of the former is replaced by 7630 $(FeCl_3)$.

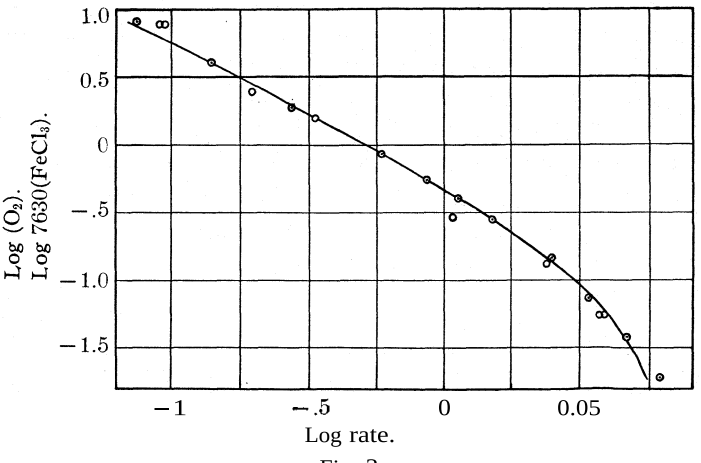

Fig. 3.

In Fig. 3 the logarithms of the rates are plotted against the logarithms of the oxygen pressures and also against the logarithms of 7630 times the ferric chloride concentrations. The curve represents both empirical equations, while the circles are the measured values with ferric chloride and the dot-centered circles are the measured values with oxygen. This graph shows that the empirical equations are in agreement with the experimental measurements.

There is no measurable dark reaction at room temperature unless both iron salts and oxygen are present at the same time, and this was not the case in any of the above experiments.

Temperature Coefficient.—The same solution was used for measuring the rate at both temperatures. Two thermostats, one at 25 and the other at 35° were arranged so that water from either could be circulated through the water jacket of the reaction chamber. The rate was measured at 25, then at 35 and then again at 25°. The manometer was always read with the solution at 25° to avoid any effect of the change of solubility of carbon dioxide with temperature. Five minutes were allowed for the temperature of the solution to come to that of the thermostat, both before reading the manometer and before turning on the x-rays. The solutions used were 0.1164 *M* $HgCl_2$, 0.290 *M* $K_2C_2O_4$, 0.2327 M KCl, all free from oxygen. Two separate measurements gave the temperature coefficient as 1.54 and 1.51 for ten degrees.

Energy Efficiency and Chain Length.—The power absorbed by the calorimeter was I^2R or $0.00155^2 \times 20.6$. This is 4.94×10^{-5} watt or 0.00071 cal./min. Since the reaction vessel containing 50 cc. of solution was 6.8 cm. long, the cross section of the solution would be 7.35 sq. cm. The area of the lead disk was 4.91 $cm.^2$ and therefore the cross section of the solution was 1.50 times the area of the lead disk, so that the power entering the solution was 0.00106 cal./min. In Table I, the amount reacting during the first minute was 0.0008 mole. This gives the energy efficiency as 1.32 cal./mole or in other units 0.91×10^{-16} ergs per molecule. Since it takes 35 volts or 56×10^{-12} ergs on the average to produce an ion pair, there were 6×10^5 molecules reacting per ion pair. It is assumed that the total energy absorbed goes into ionization.

Summary and Conclusions

The rate of the reaction under all conditions studied is given by the following equation

$$\frac{dx}{dt} = \frac{k(HgCl_2C_2O_4^{=})}{0.0823 + (O_2) + 7630(FeCl_3)}$$

where $HgCl_2C_2O_4^{=} = 0.01\,(HgCl_2)(C_2O_4^{=})$. This is for constant energy input. The oxygen concentration is in centimeters pressure, while the other concentrations are in moles per liter. In all cases studied the incident radiation was constant and totally absorbed. This equation expresses the rate only when oxygen and ferric chloride are not both present at the same time. In that case, there is also an induced dark reaction[2] which must be added to this.

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[2] **W. E. Roseveare** and **A. R.** Olson, This Journal, 51, 1717 (1929).

The great energy efficiency indicates that it is a chain reaction. The denominators of the above equations are similar to those found by Bäckstrom[3] to express the negative catalysis of alcohols in the oxidation of sodium sulfite which is a chain reaction. The effect of oxygen and ferric chloride can best be explained by Bäckström's theory that the effect of the negative catalyst is to break the chains.

It seems probable that the primary step is the decomposition of the complex according to this equation

$$HgCl_2C_2O_4^{=} + \text{energy} = HgCl + Cl^- + C_2O_4^-$$

The half-oxidized oxalate, $C_2O_4^-$, would then reduce the $HgCl_4$ in another $HgCl_2C_2O_4^{=}$ and the energy of reaction may cause the oxalate ion in the complex to decompose, giving products which may react in the same way as the half-oxidized oxalate. These chains would end if the intermediate products were oxidized by either oxygen or ferric chloride. Such a mechanism is in agreement with the above experimental equation for the rate of reaction.

The observed temperature coefficient will be the sum of the temperature coefficients for the reaction and for the dissociation of the complex ions.

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A METHOD FOR DETERMINING THE VISCOSITY OF CORROSIVE GASES AND THE MOLECULAR DIAMETER OF NITROGEN PENTOXIDE

BY HENRY EYRING AND G. A. VAN VALKENBURGH

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Introduction

The decomposition of nitrogen pentoxide has been much studied during the past few years in connection with the subject of reaction rates as it is one of the few, and of these the oldest of, unimolecular reactions. In papers dealing with the kinetics of the nitrogen pentoxide reaction, it has ordinarily been assumed to have a molecular diameter of 10^{-7} cm. Recent calculations by Tolman, Yost and Dickinson[1] and by Lewis[2] show that in order for it to be activated sufficiently rapidly it should have the extraordinarily large diameter of 6.07×10^{-6} cm. In this case one of the molecules is activated, which may greatly modify its effective diameter. It seems of interest, however, to determine this value by viscosity measurements.

[3] *H. N. Alvea and H. L. J.* Backstrom, THIS JOURNAL, **51,** 90 (1929).

[1] Tolman, Yost *and* Dickinson, Proc. *Nat. Acad. Sci.,* 13, 188 (1927).

[2] *Bernard* Lewis, Science, ***66,*** 331 (1927).

Experimental

A diagram of the apparatus is shown in Fig. 1. It was made entirely of pyrex glass without stopcocks. The nitrogen pentoxide at a pressure of 51 mm., in A, passed through the capillary D and was condensed by liquid air in the U-tube E. Nitrogen pentoxide was introduced into A, before beginning the measurements, by vacuum distillation from a mixture of white fuming nitric acid and phosphorus pentoxide, contained in a glass vessel sealed to B. The nitrogen pentoxide in some experiments was condensed in A by liquid air, in others by a mixture of ice and brine. During the distillation a low pressure was maintained by pumps at both J and H. After sufficient nitrogen pentoxide had accumulated in **A,** the arm B was sealed off, the cooling bath removed from A and evacuation at J continued until the nitrogen pentoxide crystals were colorless. The cooling bath was then applied to **A** and the arm J sealed off. The cooling bath at A was now replaced by a large Dewar containing clean ice, which maintained a temperature of 0° to within 0 1° throughout the remainder of the experiment. A water pump circulated water from a refrigerator through the cooling jacket C. A thermometer showed this temperature to be constant at 4° to within less than 0.5" during all experiments. The cooling jacket was wrapped with asbestos. The low temperature prevented decomposition of the nitrogen pentoxide while passing through the capillary.

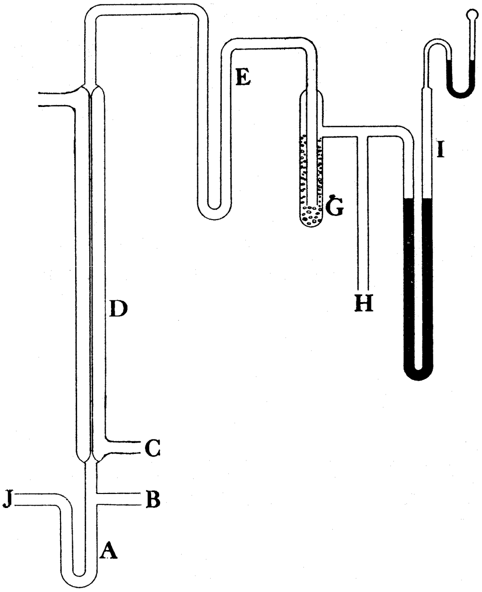

Fig. 1.—Apparatus for measuring the viscosity of a corrosive gas.

After the nitrogen pentoxide had been passing through the capillary and into the soda lime at G for from two to three hours, liquid air was applied to the U-tube at E and the time accurately noted. The high vacuum pump at H maintained a vacuum better than 0.1 mm. at all times, as shown by the mercury gage I. After nitrogen pentoxide had been condensing in E for two hours the two arms of the U-tube were sealed off at E. The exact time the left arm was sealed off was noted.

The sealed U-tube containing the nitrogen pentoxide was broken beneath the surface of standardized sodium hydroxide by pushing the two arms together. The sodium hydroxide filled the two evacuated arms, reacting with the nitrogen peritoxide without loss. The two arms were then carefully washed and the sodium hydroxide back-titrated with hydrochloric acid.

The variation of 0.1° in the ice-bath A results in a change in the vapor pressure of 0.5 mm. in a total pressure of 51 mm.[3] The amount of nitrogen pentoxide collected in unit time did not vary with a many-fold change in the surface of nitrogen pentoxide, proving that the pressure of nitrogen pentoxide in A did not lag appreciably behind the equilibrium pressure during the experiments.

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[3] Daniels and Bright, THIS JOURNAL, 42, 1131 (1920).

The capillary was standardized by passing definite volumes of nitrogen and oxygen through the apparatus under a small constant pressure. The pressure was maintained by a short column of mercury with gas on both ends held together by surface tension. The method is described by A. O. Rankine.[4] The modification used is here described. To the U-tube A a three-way stopcock was connected. One of the arms of the stopcock connected with a flask containing the purified gas. The remaining arm connected with a 6-mm. glass tube of the same length as the capillary and parallel to it. This tube was cooled by a cold water jacket in series with the cooling jacket C. Inside this tube was a column of mercury about 2 cm. long which descended in the tube as the gas escaped through the capillary D. This maintained a constant pressure on the escaping gas, depending only on the length of the column since the tube was open to the atmosphere above the column and also at the tube H. The mercury column moved between two lines on the tube, thus always expelling a known volume of gas, and the corresponding time was noted. It could be forced back up the tube for another experiment by turning the three-way stopcock to connect the tube with the flask and then carefully manipulating the adjustable manometer. The cross sectional area of the tube containing the mercury column was determined by measuring its length and then weighing it. The tube was of very uniform borebetween the marks, which were a meter apart. The volume between the marks was found to be 7.63 cc. After each series of experiments the column was forced up into a short auxiliary tube which could then be removed and weighed.

Results

In the calibration experiments the pressures on ~~the capillary were~~ 740 mm. plus the pressure of the mercury column on one end and 740 mm. on the other. The gases used were air and oxygen and in each experiment the time t_1 taken for the mercury column to move through one meter, expelling 7.63 cc. at 4°, was noted. From the data one can calculate what volume of air and oxygen, respectively, would be expelled in the time t_1 if the pressure on one end of the capillary were 51 mm. and on the other approximately zero, as in the nitrogen pentoxide experiment. Poiseuille's equation may be written

$$\frac{V}{t} = \frac{\pi r^4}{8\eta}\frac{dp}{dx} \tag{1}$$

where t is the time, r is the radius of the capillary, η is the viscosity and V is the volume of gas which passes at the point where the rate of change of pressure with distance is dp/dx. Using the gas law we have $V = nRT/p = k/p$; making this substitution for V in (1) and integrating, we obtain $p^2 = 16\eta kx/\pi r^4 t$, providing we suppose p to be zero when $x = 0$.

Thus if a capillary of uniform bore is considered in which the pressure at one end is zero and at the other $740 + a$, the ratio of the lengths of the segments L_1 in which the pressure drops from $740 + a$ to 740 mm. to the segment L_2 in which it drops from 51 to zero is

$$\frac{L_1}{L_2} = \frac{(740 + a)^2 - 740^2}{51^2} = a\left(\frac{1480 + a}{51^2}\right)$$

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[4] A. O. Rankine, *Proc. Roy. Soc.* (London), **83,** 516 (1910).

The same number of molecules would stream through these two segments in equal time. For two segments of the same length with the respective pressure drops 740 + a to 740 mm. and a second of 51 to zero mm., the number of molecules N_1 and N_2 emitted in equal times will be in the ratio

$$\frac{N_1}{N_2} = \frac{L_1}{L_2} = a\left(\frac{1480 + a}{51^2}\right)$$

and

$$\frac{V_1}{V_2} = a\,\frac{(1480 + a)}{51^2} \times \frac{15}{(740 + a)}$$

where V_1 and V_2 are the volumes passing through in the time $t_1 = t_2$. Here the volumes are measured at the high pressure ends of the capillary. In every case, V_1 was 7.63 cc. If V_3 is the volume of nitrogen pentoxide which streams through the same capillary in time t_3 when the pressure on one end is 51 mm. and zero on the other, we write

$$\frac{\eta_3}{\eta_1} = \frac{V_2/t_2}{V_3/t_3} = \frac{V_1 t_3}{V_3 t_1}\,\frac{(740 + a)}{(1480 + a)}\,\frac{51}{a}$$

where η_3 is the viscosity of nitrogen pentoxide and η_1 is the viscosity of air or oxygen.

Any two molecular diameters σ_1 and σ_3 are in the ratio $\sigma_3/\sigma_1 = M_3^{1/4}\eta_1^{1/2}/M_1^{1/4}\eta_3^{1/4}$, where M_1 and M_3 are the corresponding molecular weights. Thus

$$\sigma_3 = M_3^{1/4}\sqrt{\frac{V_3}{t_3}}\left(\frac{\sigma_1}{M_1^{1/4}}\right)\sqrt{\frac{t_1(1480 + a)a}{V_1(740 + a)51}}$$

The following table gives the data for the calibration runs.

TABLE I

EXPERIMENTAL CALCULATION

Gas	V_1	t_1	a	b	$c \times 10^{-8}$
Air	7.63	379.8	17.63	0.1719	7.81
Air	7.63	337.4	19.88	.1715	7.82
Air	7.63	343.2	19.65	.1713	7.83
O_2	7.63	340.9	22.25	.1613	7.72
O_2	7.63	198.3	37.78	.1630	7.63
O_2	7.63	339.3	22.50	.1611	7.73
O_2	7.63	211.5	33.90	.1668	7.49
			Average		7.72

In the table, V_1 is in cc., t_1 in seconds and a in mm. and $b = \sqrt{\frac{t_1}{V_1}\frac{(1480 + a)a}{(740 + a)51}}$ and $c = \frac{\sigma_1}{M_1^{1/4}}$ b. For oxygen σ_1 is taken equal to 2.96×10^{-8} and for air 3.10×10^{-8}. The other quantities have been defined.

Nitrogen pentoxide was permitted to run for 7200 seconds in five experiments, giving volumes V_3 of nitrogen pentoxide calculated to 51 mm. and 4° shown in Table II.

TABLE II

RESULTS OF EXPERIMENTS

Gas	V_3	$\sqrt{V_3/t_3}$	$\sigma_3 \times 10^8$
Nitrogen pentoxide	805	0.334	8.33
Nitrogen pentoxide	793	.332	8.26
Nitrogen pentoxide	905	.354	8.80
Nitrogen pentoxide	916	.356	8.67
Nitrogen pentoxide	804	336	8.33
		Average	8.53

Thus the average value for the molecular diameter of nitrogen pentoxide is 8.53×10^{-8}.

Discussion of Possible Errors

When a column of mercury descends in a tube it encounters a viscous resistance which might appreciably reduce the pressure on the gas escaping through the capillary. A simple calculation shows that this was not the case in the above calibration. In a typical experiment the length of the mercury column was 1.79 cm. and its radius was 0.1537 cm. The volume swept out was 7.63 cc., the time 379.8 sec.; the viscosity of mercury at 20° is 0.01589. Substitution of these values in Poiseuille's equation gives a viscous resisting pressure due to the descent of the mercury column itself of 24.8 dynes. This is to be deducted from the pressure due to the mercury column, which is 23,800 dynes. The viscous resistance is thus negligible.

In the experiment with nitrogen pentoxide the pressure at the end of the capillary next to the liquid air was low. The kinetic theory for viscosity applies only for pressures such that the mean free path is small compared with the diameter of the capillary. From the rate with which air flowed through the capillary its mean diameter was found to be 0.0294 cm. The molecular diameter is found to be 8.53×10^{-8} cm., so that the nitrogen pentoxide molecules will have a mean free path of 0.029 cm. at a pressure of 0.04 mm. Even if the resistance to flow should drop to zero for the last 0.04 mm. of the 51-mm. pressure drop or rise to ten times the value from the kinetic theory, this error should be small. Actually, a pressure of nitrogen pentoxide as low as 0.04 mm. was never reached since the space @ was evacuated only by a Hyvac pump and the pressure of permanent gas as shown by the manometer I was only kept less than 0.1 mm. This small residual pressure also lessened any chance of distillation of nitrogen pentoxide from E to G. Actually, all the nitrogen pentoxide was observed to condense on the first centimeter or two submerged in liquid air, leaving a path about ten time as long through the cooled tube on which there was no visible condensate.

The gas emerges from the capillary with an axial velocity. Thus a part of the pressure drop is not used in overcoming viscous resistance. In the calibration experiments, since the increase in volume, and therefore velocity, is less than in the nitrogen pentoxide experiments, it will be sufficient to show that for nitrogen pentoxide the energy used in communicating velocity is only a small fraction of that used in overcoming viscous resistance. If the pressure at the low pressure end be taken as 0.1 mm., the velocity will be such as to use up less than **0.3%** of the 51-mm. pressure drop. This figure is an upper limit to this error.

Conclusions

An experimental arrangement for measuring viscosities of corrosive gases is described.

The molecular diameter of nitrogen pentoxide is found to be 8.53×10^{-8} cm.

[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

OXIDATION-REDUCTION POTENTIALS. II. THE MANGANESE DIOXIDE ELECTRODES

BY STEPHEN POPOFF, J. A. RIDDICK AND W. W. BECKER

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The standard oxidation–reduction potential of the permanganate–hydrogen–manganous ion electrode is of considerable importance both from the point of view of reliable electromotive force constants and from its use in making suitable predictions. Since it is not possible to measure directly the foregoing potential, one must resort to calculations involving electromotive force measurements of the cells

$$\mathrm{Pt} \mid \mathrm{H_2, H^+} \mid \mathrm{H^+ + MnO_4^- + MnO_2} \mid \mathrm{Pt, and} \qquad \text{(A)}$$

$$\mathrm{Pt} \mid \mathrm{H_2, H^+} \mid \mathrm{H^+ + Mn^{++} + MnO_2} \mid \mathrm{Pt} \qquad \text{(B)}$$

If E_A and E_B represent the standard oxidation–reduction potentials of Cells A and B, respectively, then the standard oxidation–reduction potential (E_C) of the cell

$$\mathrm{Pt} \mid \mathrm{H_P, H^+} \mid \mathrm{H^+ + Mn^{++} + MnO_4^-} \mid \mathrm{Pt} \qquad \text{(C)}$$

can be calculated from the equation $(3E_A + 2E_B)/5 = E_C$. This calculation was made using the value of E_A obtained by Brown and Tefft,[1] and the value of E_B obtained by Tower.[2] It was noted, however, that Brown and Tefft employed chemically prepared manganese dioxide which analyzed over 99%, while Tower employed electrolytically prepared manganese dioxide whose analysis was not given. It was further observed that the potentials with electrolytic manganese dioxide varied according to the current density employed in its preparation and that the values in the literature for the potential of the manganese dioxide–permanganate electrode differed by more than 0.1 volt.

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[1] Brown and Tefft, THIS JOURNAL, 48, 1128 (1926).

[2] Tower, *Z. physik. Chem.*, 32, 566 (1900).

It was therefore deemed necessary to determine the potentials of the cells A and B employing the same kind of manganese dioxide and making a critical analysis of all the constituents entering into the reactions. As a result of this study one is led to conclude that cells involving the use of chemically pure manganese dioxide render themselves incapable of recording accurate electromotive forces because manganese dioxide reduces the permanganate ions, and the electrodes are irreversible in the presence of manganous and hydrogen ions. The foregoing conclusion becomes almost inevitable when one considers that the materials employed were purified using "atomic weight" technique and that two entirely different methods of analysis were resorted to in the analysis of the important constituents.

Experimental

A. Preparation of Materials

1. Potassium permanganate was twice recrystallized from the best quality salt and a solution of the salt was made in redistilled water. After standing for several weeks the clear solution was siphoned off and kept in a bottle painted with black auto enamel.

2. Water employed in this investigation was redistilled from alkaline permanganate solution.

3. Manganese Dioxide.—Two kinds of manganese dioxide were prepared. One is called chemical, the other electrolytic, for the sake of differentiation.

a. Chemical.—Brown and Tefft[1] prepared manganese dioxide by heating manganese nitrate at 160". They state that their product was over 99% pure but they give no explanation as to the composition of the remaining one per cent. Several attempts to make pure manganese dioxide were made before arriving at the following procedure. Manganous nitrate was prepared by a method similar to that used by Baxter and Hines[3] to prepare manganous bromide for use in the atomic weight of manganese. The manganous nitrate solution was evaporated until a considerable amount of a pasty mass of manganese dioxide had separated out, then poured into a large volume of cold water. The product thus obtained was very finely divided. After suitable washing, the manganese dioxide was dried, ground and then heated about a dozen times with concentrated nitric acid, each treatment being followed by heating to 160°. The product was also ground several times together with dilute nitric acid and the resulting solution decanted. The final product was heated for twenty-four hours at 160°. Analysis gave 99.62% of manganese dioxide and 0.41% of water.

b. Electrolytic.—Most of the literature on the electrolytic deposition of manganese dioxide deals with attempts to deposit manganese quantitatively from solution; no attempts have been made to deposit pure manganese dioxide. The adhering deposit was usually ignited to Mn_3O_4 and weighed as such; all investigators found that the product deposited does not have the formula MnO_2 In this investigation a platinum dish (100 cc.) and disk (5 cm. in diameter) served as the cathode and anode, respectively. The current density, temperature and the concentration of nitric acid were varied. The highest percentage of manganese dioxide found by the electrolytic method was about 92%, the rest being water and lower oxide of manganese. The analysis was made after the product of electrolysis was washed, dried at 160°, ground and again heated to 160° for one hour.

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[3] Baxter and Hines, THIS JOURNAL, 28, 1560 (1906).

4. Perchloric Acid.—G. Frederick Smith's 72% perchloric acid was redistilled under reduced pressure in an all-glass distillation apparatus, rejecting the first and the last quarter portion. From the redistilled portions the dilute acids were prepared.

5. Manganous perchlorate was prepared by a method similar to that used in the preparation of manganous nitrate.

B. Apparatus

The electrode vessels, the potentiometric equipment, etc., employed were those used in an earlier investigation by Popoff and Kunz.[4] About 2 g. of manganese dioxide was placed in chamber A. This was sufficient partly to cover the platinum foil.

C. Analytical Methods

1. The potassium permanganate solutions were standardized against Bureau of Standards sodium oxalate using McBride's[5] conditions but employing weight burets and electrometric methods of obtaining the end-points.

2. Perchloric acid was standardized against a sodium hydroxide solution (free from carbonates) which had been in turn standardized against constant-boiling hydrochloric acid and benzoic acid. The maximum deviations were never more than 0.05%. The total acidity of the permanganate solutions as well as that of the standard acids was checked employing the electrometric method described by Popoff and McHenry.[6]

3. The water content of the manganese dioxide was determined by heating the products in a fused silica combustion tube to 900° in a current of dry oxygen and absorbing the water in a suitable bottle containing dehydrite.

4. The manganese dioxide was analyzed by the following methods.

a. The ferrous sulfate method consisted in adding an excess of the acidified reagent to the manganese dioxide, heating until all of the manganese dioxide had dissolved and then titrating the excess with standard permanganate solution. This method was found convenient for determining the oxidizing power of the electrolytic but not of the chemically prepared manganese dioxide. The latter required heating from thirty to forty-five minutes near the boiling point in order to accomplish the complete reduction. Duplicates failed to agree either among themselves or against the sodium oxalate method when employing the chemical manganese dioxide. Good agreements, however, were found when employing the electrolytic manganese dioxide.

b. The sodium oxalate method consisted in adding an excess of sodium oxalate to 50 cc. of 9 N sulfuric acid containing about 0.1 g. of manganese dioxide. then keeping the solution at about 90° (for about five minutes) until reduction was complete. Finally, after diluting to 250 cc., the excess sodium oxalate was titrated with standard permanganate solution. In the actual analysis it was deemed necessary to employ about 0.5 g. of manganese dioxide and after suitable dilution to titrate an aliquot portion. A sample of Bureau of Standards pyrolusite containing an oxidizing equivalent of 87.53% in terms of MnO_2 was found by the foregoing method to be 87.74%. Considering that the sample contained iron, copper and about 5% of insoluble matter, which were not removed, the sodium oxalate method gave good results.

c. The Pyrophosphate Method.—The dioxide was dissolved in hydrochloric acid, the solution was heated to the boiling point, then about 2 g. of monoammonium phosphate were added, followed by freshly distilled ammonia until the solution smelled of ammonia. The solution was continually stirred until the precipitate had been converted to the silky form. This was followed by digestion for about two hours. After cooling, the

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[4] Popoff and Kunz, THIS JOURNAL, 51,382 (1929).

[5] McBride, *ibid.*, 34, 393 (1912).

[6] Popoff and McHenry, *Ind. Eng. Chem.*, 20, 534 (1928).

precipitate was filtered, washed with water and finally heated at about 800° to constant weight. The filtrate was evaporated to a small volume and the manganese was determined colorimetrically after oxidation to permanganate by potassium periodate, following the usual procedure. By this latter procedure a correction was made for the solubility of the manganese ammonium phosphate—thus rendering the method precise and accurate.

The effect of varying the current density and the concentration of nitric acid in the electrolytic method of preparing manganese dioxide is seen from the results given in Table I.

TABLE I

ANALYSIS OF ELECTROLYTIC MANGANESE DIOXIDE

HNO_3 added, cc.	MnO_2, %		H_2O, %	Lower oxides, %	CD_{100}	Method of analysis
2	91.49	91.34	5.29	3.30	0.05	ferrous iron
2	90.85	90.87	5.07	4.08	.03	Ferrous iron
2	90.57	90.79	5.03	4.29	.10	Ferrous iron
5	91.57	91.67	5.00	3.38	.05	Sodium oxalate
10	90.00	89.98	4.72	5.28	.05	Sodium oxalate

The effect of increased temperature, different acids added, such as formic, perchloric, gave manganese dioxide differing in oxidizing power but slightly from the foregoing. Table II gives the comparison as well as the results of analyses of the different kinds of manganese dioxide by two entirely different methods.

TABLE II

ANALYSES OF MANGANESE DIOXIDE BY DIFFERENT METHODS

Kind of MnO_2	MnO_2 from oxalate, %	MnO_2 from $Mn_2P_2O_7$, %	H_2O, %	Total	
				From oxal.	From $Mn_2P_2O_7$
Commercial	89.55	95.60	..	...	...
	89.73	95.80			
Electrolytic	91.57	97.18	5.00	96.57	102.18
	91.67	97.49	5.00	96.67	102.49
Chemical	99.62	99.59	0.41	100.03	100.00

It is believed that there are no lower oxides of manganese present in our chemically prepared manganese dioxide, as the percentages of manganese dioxide found by two entirely different methods are in excellent agreement.

5. The manganous perchlorate solutions were analyzed by the pyrophosphate method given under manganese dioxide. The mean error was of the order of 0.03%.

D. The Instability of Potassium Permanganate Solutions

The instability of potassium permanganate in perchloric acid solutions in the presence and absence of manganese dioxide is a very significant and important factor in this investigation. It is very evident from Table III that permanganate solutions are decomposed by comparatively dilute perchloric acid solutions either in the presence or absence of pure manganese dioxide. In the presence of the electrolytic manganese dioxide, a 0.00237 M potassium permanganate solution in 0.025 M perchloric acid became practically colorless in about three days. It is significant to note that a solution (No. 4) identical with the one employed by Brown and Tefft was found to have undergone considerable decomposition, although it gave almost an identical value for the electromotive force of the cell. A solution (No. 5) identical with No. 4 was prepared, sealed in a glass vessel and kept in the constant temperature bath for seven days. This solution also underwent decomposition, thus proving that outside contamination was not responsible for the decomposition.

The instability of potassium permanganate solutions in the presence of sulfuric acid is of about the same order as that found in perchloric acid.

TABLE III

INSTABILITY OF POTASSIUM PERMANGANATE SOLUTIONS

No.	Acid and concn.	Concn. $KMnO_4$ found, per g. of soln.	Loss, mg.	No. of days	
1	$0.5M$ $HClO_4$	0.001587	0.022	0	
		.001575	.034	1	
		.001556	.053	2	
		.001526	.083	3	
2	0.025 M $HClO_4$	.04938		0	
		.04929	.09	1	
		.04923	.15	2	
		.04919	.19	3	
3	0.025 M $HClO_4$ with MnO_2, Series I, Cell 1	.001556	,059	0	
		.001497		8	
4	$0.025M$ $HClO_4$ with MnO_2, Series IV, Cell 2	.0003683	.034	2	Brown-Tefft soln.
		.0003342			
5	$0.025M$ $HClO_4$ with MnO_2, sealed	.0003683	.052	7	
		.0003162			

E. Electromotive Force Measurements

Electromotive force measurements were made of Cells A and B under varying conditions. It is evident that it is next to impossible to obtain accurate electromotive force data from Cells **A** (Series I–IV) because of the instability of the potassium permanganate solution. It is interesting to note that the cells in Series IV gave 1.4972 and 1.4977 volts as compared to 1.4975 obtained by Brown and Tefft. These authors state that "the potential of a newly prepared manganese dioxide electrode, when first filled with perchloric acid–permanganate mixture rose at first, then declined, approaching a limiting value after several weeks. According to analysis, this drop in potential was not due to the decomposition of the potassium permanganate." It is significant to note further that Inglis,[7] who employed electrolytic manganese dioxide, states that the coating on

[7] Inglis, *Z. Elektrochem.*, 9, 222 (1903).

the electrode must be very thin in order to obtain reproducible results. The solubility of the electrolytic manganese dioxide is much greater than that of the chemically pure manganese dioxide. It is doubtful whether or not the solution was saturated with the manganese dioxide when the electrolytic manganese dioxide was employed by former investigators.

TABLE IV

ELECTROMOTIVE FORCE MEASUREMENTS

Series I, $KMnO_4$, 0.01 *M;* $HClO_4$, 0.0250 *M.* Chemical MnO_2, 99.6%

Time	Volts Cell 1	 Cell 2	Remarks
9:00 A. M.	1.5162	1.5141	Plain platinum electrodes in graded seal glass
2:00 P. M.	1.5165	1.5140	
6:00 P. M.	1.5166	1.5141	
10.00 A. M.	1.5175	1.5141	
2.00 P. M.	1.5176	1.5143	
9:00 A. M.	1.5041	1.5000	New electrodes of plain platinum foil, sealed in lead glass
3:00 P. M.	1.5031	1.5038	
10:00 A. M.	....	1.5075	
1:30 P. M.	....	1.5078	
10:00 A. M.	....	1.5096	
3:00 P. M.	....	1.5098	

$KMnO_4$ solution changed from 0.001556 to 0.001497 in eight days.

Series II. Same as Series I, except MnO_2 (chemical) on Pt electrodes

Time	Volts Cell 1	 Cell 2	Remarks
10:00 A. M.	1.5029	1.5002	
1:00 P. M	1.5000	1.5001	MnO_2 electrodes interchanged
7:00 P. M.	1.4979	1.5001	
9:30 A. M.	1.4966	1.4980	
11:30 A. M.	1.4968	1.4986	
4:30 P. M.	1.4968	1.4986	
10:00 A. M.	1.4951	1.4973	E. m. f. lower than in Series I and continually decreasing
1:00 P. M.	1.4951	1.4975	
7:00 P. M.	1.4963	1.4983	
9:00 A. M.	1.4936	1.4959	
1:00 A. M.	1.4938	1.4959	
7:00 P. M.	1.4932	1.4952	

Series III. $KMnO_4$, 0.00237 *M;* $HClO_4$, 0.025 *M;* Electrolytic MnO_2

Time	Volts Cell 1	Remarks
10:00 A. M.	1.4735	
1:00 P. M.	1.4747	
7:00 P. M.	1.4737	
7:00 P. M.	1.4569	Three-day interval; the solution became almost colorless
8:00 P. M.	1.4567	
4:00 P. M.	1.4533	
5:00 P. M.	1.4522	

TABLE IV (*Concluded*)

Series IV. Same as Series III except Chemical MnO_2, 99.6%

Time	Cell 1	Cell 2	Remarks
7:00 P. M.	15068	1.5071	
11:30 A. M.	1.5077	1.5107	
4:00 P. M.	1.5075	1.5089	
8:00 P. M.	1.4815	1.4770	Electrodes cleaned with H_2O_2–H_2SO_4 mixture
10:00 A. M.	1.4896	1.4882	
1:30 P. M.	1.4910	1.4886	
9:00 A. M.	1 4956	1.4949	
1:00 P. M.	1.4966	1.4967	Solution changed (Cell 2) from 0.0003683 to 0.0003343
4:00 P. M.	1.4970	1.4965	
7:00 P. M.	1.4972	1.4977	

Brown and **Tefft** found 1.4975.

Series **V**. $Mn(ClO_4)_2$ in $HClO_4$ soln. Chemical MnO_2, 97.8%, prepared by the usual method

Date	Time	E. m. f.
1/6	8:34 P. M.	1.1890
	9:10	.8955
1/7	9:15 A.M.	.8845
	11:35	.9219
	7:03 P. M.	.9258
1/9	8:30 A. M.	.9250
	10:20	.9256
	1:20 P. M.	.9252

Series **VI**. $Mn(ClO_4)_2$ in $HClO_4$ soln. Chemical MnO_2, 99.6%

Date	Time	E. m. f.	Remarks
9/1	7:45 P. M.	0.72005	
	7:49	.71563	
	7:54	.71701	
9/3	7:02 P. M.	.66450	
	7:35	.64057	Stirred
	9:05	.63316	
	11:00	.63511	Stirred
9/9	2:55 P. M.	.62416	Stirred
	4:00	.62409	Stirred
	5:18	.63336	
9/10	2:45 P. M.	.69062	Stirred by motor
	4:30	.75642	Stirred by motor
	4:40	.73809	
	4:55	.70818	

Series V and VI give the electromotive forces obtained employing Cell B. When manganese dioxide (97.8%), prepared by the usual method, and containing lower oxides, was used (Series V), a steady potential was obtained in about two days. However, with the pure (99.6%) manganese dioxide the potentials were unsteady and subject to change without any notice.

After presenting this article for publication, opportunity was given to look over and examine the article of Brown and Liebhafsky.[8] The main argument is the preparation and analysis of the manganese dioxide. We were not able to prepare pure manganese dioxide until the pasty mass was dropped into cold water, this procedure giving a crystalline product. Two entirely different and specifically stated methods of analysis showed that the manganese dioxide prepared did not contain lower oxides of manganese than that corresponding to MnO_2. The foregoing authors do not give any details of their method of analysis. Without modification of the method of the preparation of the manganese dioxide, the product gave a steady potential in a few days as shown in Table IV, Series V. In Table IV, Series VI, it has been shown that pure manganese dioxide does not give steady potentials even if the electrode solution is stirred and left to stand for a period of nine days. If one employs the values of E_A and E_B, and calculates E_C, one obtains a value of -1.48 volts. Brown and Liebhafsky report a value of -1.446 using the new value of E_B rather than that obtained by Tower. One would expect a much larger difference and in the opposite direction in the calculated values, since Tower used electrolytic manganese dioxide, which everyone admits contains lower oxides of manganese.

It is significant to note that, in general, serious polarization[9] may be expected to take place at electrodes which involve reactions that take place with a change in the oxygen content. All of the electrode potentials E_A, E_B and E_C certainly involve a change in the oxygen content and therefore one must resort to other means than electromotive force measurements of determining these electrode potentials.

Summary and Conclusions

1. Pure manganese dioxide (99.6%, rest water) was prepared and analyzed by two entirely different methods.

2. It was not possible to prepare electrolytically manganese dioxide which did not contain lower oxides of manganese.

3. Solutions of potassium permanganate containing perchloric acid were found to be unstable either in the presence or absence of manganese dioxide.

4. Due to the foregoing instability, it was found impossible to measure the potential of the permanganate–hydrogen–manganese dioxide electrode.

5. When pure manganese dioxide was employed in the manganese dioxide–hydrogen–manganous electrode, the electrode was found to be irreversible.

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[8] Brown and Liebhafsky, THIS JOURNAL, 52, 2595 (1930).

[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co. Inc., New York, 1923, p. 388.

6. It is evident then that the potential of the permanganate–hydrogen–manganous electrode cannot be calculated from the potentials of the manganese dioxide electrodes.

7. Since the manganese dioxide electrodes involve reactions in which there are changes in the oxygen contents, one would expect polarization to take place at the electrodes.

8. Specific directions are given for the precise determination of manganese gravimetrically.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

TRANSFERENCE PHENOMENA AND THE EXISTENCE OF COMPLEX IONS AS INTERPRETED BY THEIR MAGNETO-CHEMICAL BEHAVIOR

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For our purpose we shall define a molecule as an entity consisting of atoms which are held together by chemical bonds. By a chemical bond we shall mean a coupling of the spin magnetic moments of a pair of equivalent electrons[1] which are held in common by two atoms. Sodium chloride, from this point of view, does not consist of molecules in the crystalline state but of sodium ions and chloride ions. On the other hand, mercuric chloride consists mostly of molecules in both the crystalline state and in solution. Hydrogen consists of molecules in the gaseous state and in the liquid.[2]

We shall extend this definition to a molecular ion. It is an ion whose atomic constituents are coupled by means of chemical bonds. We shall identify complex ions with molecular ions.

Let us consider the familiar example of the ferricyanide ion. Ferric ion in solution is strongly paramagnetic with a molal susceptibility which corresponds to five Bohr magnetons, that is, it appears to have five unbalanced electrons. If we add cyanide ion to it there is an immediate drop in its magnetic susceptibility and the resulting ferricyanide ion possesses a susceptibility corresponding to about one Bohr magneton. The magnetic moments of unbalanced electrons have been neutralized. It is natural to conclude that a number of chemical bonds have been created, that is, that a true complex (molecular) ion has been formed. It has long been recog-

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[1] Lewis, "Valence and the Structure of Atoms and Molecules," American Chemical Society Monograph Series, The Chemical Catalog Co., New York, **1923**; Heitler and London, *Z. Physik,* **44**, 455–472 (1927); Heitler, *ibid.,* **47**, 835–858 (1928); London, *ibid.,* **46**, 455–477 (1928); *Naturwiss.,* **16**, 58–59 (1928).

[2] McLennan and McLeod, *Nature,* **123**, 160 (1929).

nized[3,4] that paramagnetic ions suffer a drop in their susceptibilities upon entering into complex ions.

Ordinarily, then, we should expect complex ions to form very readily whenever the metallic ion contains unbalanced electrons, that is, if it is paramagnetic. It is well known that diamagnetic ions, such as Cu^+, Zn^{++}, Ag^+, etc., form complex ions. These ions, although they are diamagnetic, are next to the paramagnetic ions in the periodic system. Their last complete electronic shells are not extremely stable (as is shown by the ease with which an electron may be removed from cuprous to form cupric ion; trivalent silver appears to exist, and trivalent gold is well known). The balance in the magnetic moments may be disrupted (the ion may become activated) and then they may recouple with other ions, such as cyanide, and produce complex ions.

In the case of such ions as sodium, potassium, magnesium, etc., whose outer electronic configurations are similar to those of the rare gases preceding the neutral atoms in the periodic table, there is no chemical evidence for their participating in complex ion formation. (In the gaseous state their electronic configurations are even more stable than those of the corresponding rare gases because the additional positive charge on the kernel attracts the electrons in the outermost shell more strongly.)

However, McBain and Van Rysselberge[5] have interpreted transference phenomena as evidence for the general existence of complex ions even among "rare gas" ions. They found, for example, that in a 0.05 M $MgSO_4$ and 0.95 *M* $(NH_4)_2SO_4$ solution the magnesium had actually migrated with the negative current. In a solution of 0.05 *M* $CaCl_2$ in 4 M NH_4Cl there appeared no net migration of the calcium ion with the positive current. They concluded that this behavior was similar to that of ferrous ion in the presence of cyanide ion and that Ca^{++}, Mg^{++}, etc., existed to a large extent in the form of complex ions. They argued from this "anomalous" electrolytic migration that undissociated molecules exist even in dilute solutions of such salts as $MgSO_4$, $CaCl_2$, etc., and hence that theories which postulate complete dissociation in such solutions are invalid.

We are reporting here a short magneto-chemical investigation which we believe will throw some light on the possibility of having such "anomalous" transference and yet having no complex ions present.

In our investigation we tried to reproduce the conditions obtaining in the work of McBain and Van Rysselberge rather closely and still make them amenable to magneto-chemical study.

Instead of magnesium sulfate we have employed manganous sulfate, with which it forms isomorphic crystals, so that those properties that are

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[3] (a) Pascal, *Ann. chim. phys.*, 16, 359 (1909); (b) 16, 520 (1909).

[4] Shaffer and Taylor, THIS JOURNAL, 48, 843 (1926).

[5] McBain and Van Rysselberge, *ibid.*, 50, 3009 (1928).

associated with the size and charge of the ions are very similar in both salts. However, manganous ion has five Bohr magnetons just as ferric ion. It has then five unbalanced electrons which presumably would be the first to couple upon the formation of a complex ion. Moreover, such a coupling would decrease the susceptibility of its solution.

If we can show that upon the addition of ammonium sulfate no change in the susceptibility of the manganous ion has occurred and if the manganous ion has shown no net migration with the positive current, then it has been demonstrated that transference need be no measure of the formation of a complex ion, that is, no chemical bonds have formed, no electromagnetic coupling of electrons has occurred, and the forces between the ions are purely electrostatic.

The coupling of magnetic spin moments, as a rule, produces a great change in the susceptibility. The relatively high concentration of complex ions which has been assumed to exist in mixed salt solutions such as those mentioned would make refined magnetic measurements unnecessary. Nevertheless, we made precise magnetic measurements by modifying the well-known Gouy method[4] so as to make it practically a null method and thereby we have been able to measure relative susceptibilities with unusual accuracy.

We shall state in advance that no change in the susceptibility of bivalent manganese was noted when it was present with ammonium sulfate, and that manganous ion did not show a net migration with the positive current (by changing the concentrations we were able to force a net migration in the opposite direction). Moreover, when we added cyanide ion and formed the well-known complex manganocyanide ion there was a radical decrease in the susceptibility.

Experimental

In order to determine the effect of 1.07 M $(NH_4)_2SO_4$ upon the susceptibility of 0.058 M $MnSO_4$, we employed the following method. The ordinary Gouy method consists in suspending a glass tube vertically from the stirrup of an analytical balance so that a horizontal glass partition at the center of the tube comes into the middle of the pole gap of a magnet. The substance to be investigated is placed in one compartment of the tube and the other compartment is usually evacuated. The change in weight observed when the magnetic field is excited depends upon the difference between the susceptibility of the substance in the upper and in the lower compartment. The action of the magnetic field upon the uniform glass tube is eliminated by having it extend to a field of negligible intensity on both sides of the pole gap.

We were interested primarily in comparing the susceptibility of the manganous ion when it was dissolved in a solution of ammonium sulfate with its susceptibility in pure water. We filled the upper compartment, therefore, with a solution of manganous sulfate in water and the lower compartment with a solution containing the same concentration of manganous sulfate in the ammonium sulfate.

The ammonium sulfate and water being diamagnetic, their effect was almost canceled out since diamagnetic susceptibilities are small and of about the same order of magnitude (per gram) for these substances. Hence, the balance would record principally any change in the susceptibility experienced by the bivalent manganese.

The pull in the magnetic field was very slight as only differences were involved and irregularities (which usually result from the tube being attracted to one side of the gap), temperature variations, etc., were eliminated. The method had most of the advantages of a null method.

We varied our procedure somewhat so as to eliminate the slight non-uniformity in the glass tube. The upper portion of the tube **A** was filled with 0.058 *M* $MnSO_4$ and it was then sealed off and a hook in the glass was made so that a string of braided silk could be **attached** to it with its other end fastened to the stirrup of an analytical balance. The lower portion was then filled with a solution of manganous sulfate of the same concentration.

The change in weight was then recorded for different amperages going through coils of the magnet. This change in weight registered the non-uniformity of the glass and its effect could be corrected for. The solution of 0.058 *M* $MnSO_4$ in 1.07 M $(NH_4)_2SO_4$ was then introduced in the lower compartment and the change in weight was observed for different currents. This procedure was repeated for a solution of 0.058 M $MnSO_4$ in 2.3 *M* KCN.

We determined the diamagnetic susceptibilities of the ammonium sulfate and potassium cyanide in separate runs employing the same method but having water in the upper compartment. In this way our results are practically independent of any impurities in our chemicals, which, however, were the purest obtainable in the market.

The same calibrated pipets, etc., were employed for all runs. The oxidation of the manganocyanide ion was avoided by pipetting the manganous sulfate into the potassium cyanide solution covered with xylene. The densities were measured with a pycnometer bottle to about 0.05%.

Magnetic Results

The change in weight of the tube produced by the magnetic field depends upon the difference between the susceptibility per unit volume of the upper portion and that of the lower portion. No pull corresponds to identical susceptibilities. In the table below the headings denote the material in the lower compartment.

TABLE I

THE PULL IN THE MAGNETIC FIELD

Amperes	I 0.058 *M* $MnSO_4$ in 1.07 M $(NH_4)_2SO_4$, mg.	II 0.058 M $MnSO_4$ in 2.3 *M* KCN, mg.	III 0.058 *M* $MnSO_4$, mg.	IV I corrected, mg.
25	0.43	15.40	0.07	0.04
30	.56	19.50	.06	.05
35	.66	22.70	.11	.06
40	.75	25.20	.10	.07
45	.82	27.25	.12	.08
50	.87	29.00	.11	.10

Column IV corresponds to Column I corrected for the difference in the susceptibilities of the water and ammonium sulfate. With our tube no change in susceptibility corresponds to Column III. The weights are probably accurate to within five or six hundredths of a milligram.

The table shows that the susceptibility of the manganous ion in the presence and in the absence of ammonium sulfate is identical within our limits of error. One-tenth of a milligram pull corresponds to a change in the susceptibility of about 0.2%.

The large pull induced by the potassium cyanide means that the susceptibility of the bivalent manganese in the solution of the cyanide has dropped enormously. In a short note[6] we calculated the molal susceptibility of the bivalent manganese in this solution as 1650×10^{-6}, whereas in the absence of the potassium cyanide it is $14{,}950 \times 10^{-6}$, a change of about nine-fold.

Transference

We carried out several electrolytic migration experiments in the usual manner employing a three-partition cell with a cadmium anode and a platinum cathode. We followed McBain and Van Rysselberge in taking equal volumes from the various compartments for comparison. The manganous ion was titrated with standardized permanganate solution in the presence of zinc sulfate. In the first series the same concentrations were employed as were tested magnetically, *i. e.*, 0.055 *M* $MnSO_4$ in 1.07 M $(NH_4)_2SO_4$. We found the same (within 0.2%) concentration in both the unchanged center and anode portions after passing seventeen milliamperes for about four hours and also after ten hours.

To test whether we could alter the conditions so that the net migration could actually be reversed, a solution containing 0.038 M Mn^{++} in 2.5 *M* $(NH_4)_2SO_4$ was electrolyzed. A net gain of about 0.6% in concentration was observed in the anode portion after passing seventeen milliamperes for twelve hours.

Discussion

The magnetic susceptibility of manganous sulfate was found[7] to be independent of the concentration. Such constancy is in itself excellent evidence that no complex ions are present. However, the susceptibility of many paramagnetic substances does vary with the concentration and among these substances chemical evidence also leads to the conclusion that complex ions are present. We shall give some examples of the numerous paramagnetic ions which show an immediate decrease in their susceptibilities as soon as they constitute a part of negative complex ions.

TABLE II

PARAMAGNETIC IONS AND NEGATIVE COMPLEX IONS

Metallic ion	Complex	Metallic ion	Complex
Fe^{++}	$[Fe_2(P_2O_7)_3]^{8-}$	Fe^{+++}	$[Fe_2(P_2O_7)_3]^{6-}$
	$[Fe(CN)_6]^{4-}$		$[Fe(PO_3)_6]^{3-}$
	$[Fe(CN)_5(NO)]^{4-}$		$[Fe(CN)_6]^{3-}$
Mn^{++}	$[Mn(CN)_6]^{4-}$		$[Fe(CN)_5(NH_3)]^{3-}$
	$[Mn_2(P_2O_7)_3]^{8-}$		$[Fe(CN)_5(NO_2)]^{3-}$
Ni^{++}	$[Ni(CN)_4]^{2-}$	Cu^{++}	$[CuBr_4]^{2-}$

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[6] Freed and Kasper, THIS JOURNAL, 52, 1012 (1930).

[7] Cabrera. Moles and Marquinas, *J. chim. phys.*, **16,** 11 (1918).

Indeed, as long ago as 1909 Pascal[11] after extensive researches on the magnetic behavior of complex ions expressed the generalization that there is a parallelism between the diminution in the analytical character (namely, the reactivity) of the metallic ion and the diminution of its magnetic susceptibility.

There is but one exception as far as we know where a paramagnetic ion does not show a marked decrease in its susceptibility when it forms a negative complex ion. This is chromic ion. Chromic ion in water, in its ammonia complex ions, and in its cyanide complexes displays nearly the same molal susceptibility.

It is highly improbable that in the case of the manganous ion we have a sulfate complex ion which would have just the same susceptibility as the manganous ion and yet its cyanide complex would have a much lower susceptibility. That is just what must occur to account for the "anomalous" transference on the assumption of complex ions and still not conflict with the magnetic behavior of the manganous ion.

Our results strongly indicate that manganous ion has not formed any magnetic bonds (any chemical bonds) with the sulfate ions. The attraction for the sulfate ions should then be regarded, with a high degree of approximation, as electrostatic only. These are the forces which Debye and Hückel considered in their famous interionic attraction theory, which postulates complete dissociation. We are inclined to believe that a comprehensive extension of their methods to concentrations which we have been employing would disclose on theoretical grounds a reversal in the direction of migration such as has been observed.

According to the interionic attraction theory every positive ion will have, on the average, a negative ion (or ions) of equal charge near it but there will be fluctuations from this average. With the types of ions that we have been considering the fluctuations will take the form of clusters of negative ions about the positive ion. The results from transference indicate that the cluster, as a whole, having an excess negative charge migrates with the negative current. The probability of this cluster is greater for those positive ions which have a greater positive charge and a smaller radius. (We realize that emphasis upon one factor is scarcely warranted because it cannot be isolated from the interacting influences which operate in so complex a phenomenon as transference, the interaction of moving charges, clusters of varying complexity and of both signs, dehydration effects, etc. However, we shall continue with our point a little further.) The fact that the net transference of magnesium ion can be reversed more readily than manganous ion and also more readily than potassium ion suggests that the reversal is a function of the charge and the radius of the ion, the very magnitudes alluded to above. It is very probable that manganous ion is somewhat larger than magnesium ion. Also potassium ion, both because of its smaller charge and because of the greater number of electrons, is larger and hence it is not altogether surprising that the migration of magnesium ion in the "wrong" direction can be forced more readily.

It is extremely probable then that ions such as Na^+, K^+, Mg^{++}, which have electronic configurations in the gaseous state like those of the rare gases retain their configurations in solution and that they do not form complex or molecular ions.

Summary

The nature of complex ions has been reviewed in terms of current theories on molecular structure as related to magnetic properties.

It has been shown that a metallic ion which does not form negative complex ions can show a net migration to the anode. It is to be concluded that the exhibition of such migration is no proof of the formation of complex ions.

A new modification of the Gouy method is described which permits the measurement of relative susceptibilities to be made easily and accurately.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE RICE INSTITUTE]

THE ATOMIC WEIGHT OF VANADIUM

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The values now accepted for the atomic weight of vanadium depend upon the determinations of McAdam,[1] and Briscoe and Little.[2] These investigators have reviewed the earlier determinations, and have pointed out serious defects in all of them. Consequently, the earlier work is not given further detailed consideration here.

McAdam, from five measurements of the $NaVO_3$–NaCl ratio, obtained the average value 50.957 for the atomic weight[3] of vanadium. Briscoe and Little, rejecting two experiments in taking the final mean, derived the value 50.955 from nine measurements of the $VOCl_3:3Ag$ ratio. While these results agree substantially, it may be mentioned that McAdam's investigation was intended only as a preliminary one, and cannot be given the same weight as that of Briscoe and Little. The general agreement between the results of the two series of experiments, however, practically excludes the possibility that the latter investigators, who used a distillation method in the purification of their vanadyl trichloride, were dealing with a constant boiling mixture.

In their determination of the $VOCl_3:3Ag$ ratio, Briscoe and Little em-

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[1] McAdam, THIS JOURNAL, 32, 1603 (1910).

[2] Briscoe and Little, J. *Chem. Soc.*, 105, 1310 (1914).

[3] The antecedent atomic weights used throughout this paper are: O = 16.000; Ag = 107.880; Cl = 35.457; Na = 22.997.

ployed the Richards nephelometric method of titration. They also introduced an entirely new technique for purifying the vanadyl trichloride by fractional distillation. The measurements were carried out with extreme care, and the results indicate that the analytical method may be used to assign a value for the atomic weight of vanadium with an error of only 0.002 or 0.003 unit. Nevertheless, an examination shows that there is a difference of 0.009 unit in the mean values of the atomic weight to be derived from the two fractions (C and D) of the material which Briscoe and Little used in their final analyses. It seems probable that at least one of these fractions contained small amounts of some impurity, possibly air, an impurity which would tend to raise the calculated values of the atomic weight.

This consideration has led us to undertake another determination of the $VOCl_3$:3Ag ratio, using the method developed by Briscoe and Little, with certain deviations: (1) phosphorus and arsenic were eliminated from the vanadium material prior to the preparation of the vanadyl trichloride; (2) ground-glass connections in the distillation apparatus were avoided, in order to prevent the introduction of air into the material; (3) half of the samples were hydrolyzed in dilute nitric acid, the other half in dilute ammonium hydroxide; (4) considerably larger samples were used for analysis, in the hope of extending the precision of the results.

Preparation of Vanadyl Trichloride.—Two pounds of vanadic oxide prepared from Peruvian patronite were obtained from the Vanadium Corporation of America for this work. The analysis of this material stated that it contained 90.75% of V_2O_5 and that it was commercially free from arsenic and phosphorus.

To insure complete removal of these impurities, we employed the following procedures, adapted from those described by McAdam.[4] The oxide was dissolved in concentrated sodium hydroxide solution and a black residue was filtered off. The solution of sodium metavanadate was concentrated and allowed to crystallize; the first small crop of crystals was rejected. The sodium metavanadate was acidified with sulfuric acid and the precipitated vanadic oxide washed with distilled water. It was reduced by warming with oxalic acid solution, and converted to the double ammonium oxalate by the addition of a slight excess of ammonium oxalate. The double salt was fractionally crystallized until it gave no test for sulfate with barium chloride. The crystals were dissolved in water and the solution precipitated with an excess of ammonium hydroxide. The precipitate of ammonium vanadite was washed several times, collected on a filter and dried. A portion of the ammonium vanadite was then mixed with recrystallized sodium carbonate and fused. This step was discontinued, however, when it was discovered that a poisonous gas[5] was liberated in the reaction. The bulk of the ammonium vanadite was treated with nitric acid and evaporated to dryness, to drive off the ammonium salts. The resulting vanadic oxide was thoroughly washed with water, dried and fused in platinum. The product was a dark red mass of crystals.

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[4] McAdam, THIS JOURNAL, 32, 1606 (1910).

[5] Probably cyanogen resulting from the incomplete removal of the ammonium oxalate. An analogous reaction is: $NH_4OOC—COONH_4 \xrightarrow{P_2O_5} 4H_2O + (CN)_2$.

The preparation of vanadyl trichloride from this material was carried out as follows. The powdered vanadium pentoxide was placed in a pyrex combustion tube contained in an electric furnace and reduced to the trioxide by heating to a dull red in a current of hydrogen. It was noted at this stage that no arsenic appeared in the cooler portions of the tube. After the tube had cooled, the hydrogen was swept out by a current of nitrogen. The nitrogen was displaced by chlorine, which reacted with the trioxide to form vanadyl trichloride when the tube was again heated.

These operations were carried out in an all-glass apparatus, the combustion tube being connected by ground-glass joints. The bulb for condensing the vanadyl trichloride was cooled in an ice-bath, and was connected to the combustion tube only after the reduction of the oxide. Of the gases which were utilized, hydrogen and chlorine were obtained from commercial tanks, while nitrogen was prepared by the reaction of sodium nitrite and ammonium chloride. The gases were washed in towers of glass beads wetted with 1:1 sodium hydroxide solution, and dried in similar towers containing 95% sulfuric acid.

When the formation of vanadyl trichloride had ended, the collection bulb was disconnected temporarily and closed with glass plugs held in place by rubber caps. The vanadic oxide regenerated in the chlorine treatment was again reduced and treated with chlorine, and a second portion of vanadyl trichloride collected in the same bulb as the first. To eliminate some of the excess chlorine in the preparation, mercury was added. The collection bulb was then exhausted by means of a suction pump and sealed off completely from the air. The final product had a red color, probably due to the presence of a small quantity of vanadium tetrachloride.

Purification of Vanadyl Trichloride

The material from the preparation described above was treated successively with mercury and with sodium in several all-glass systems, without exposure to air. The excess of chlorine in the material at this stage was not markedly decreased by contact with mercury over a period of four months, by continued exposure to sodium wire, or even by a three-hour treatment with molten sodium. The reaction with sodium, however, did remove the red color from the product.

To accomplish the removal of the excess chlorine, the bulb of vanadyl trichloride was heated to about 130° in an oil-bath, and the chlorine was permitted to escape through a small hole punctured in one of the glass capillaries of the system. When the internal pressure of the system was sufficiently reduced, the capillary was again sealed. Under these conditions practically all of the chlorine must have been driven off, while very little moisture, if any, could have entered the system.

The vanadyl trichloride was then distilled in evacuated all-glass apparatus of the type used by Baxter and Fertig[6] in their work on the atomic weight of titanium. The general procedure of distillation which was followed differed in no respect from that described by these investigators.

The essential details of the distillations proper are given in Table I. This table does not include several partial distillations which were not very effective because of the presence of excess chlorine in the material. The capital letters in Table I refer to glass bulbs of 200 to 50-cc. capacity, in which the main portion of the material was handled. The combined numerals and letters refer to the small bulbs (5 cc.) in which samples were removed for analysis. These symbols are arranged in the table in the order

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[6] Baxter and Fertig, THIS JOURNAL, 45, 1230 (1923).

in which the corresponding bulbs were sealed off from the main system. The terms "head" and "tail" are used to designate more and less volatile fractions removed during the distillation, In order to indicate the composition of different fractions of the material, we have included in the table the values for the atomic weight obtained by analysis of various samples. Volhard's method was used to determine the chlorine content of Samples A1 and **B3;** the method applied to the other samples is described in the following section of this report.

TABLE I

DISTILLATION OF VANADYL TRICHLORIDE

System no.	Fraction of $VOCl_3$	Estimated wt., g.	Type of fraction	At. wt. of vanadium
1	A1	5.5	Head	50.7
	A2	6.0	Head	
	B	167.5	Main	
	A, A3, A4	13.0	Tail	
2	C	150.5	Main	
	B, B1, B2	10.5	Tail	
	B3	6.5	Tail	51.1
3	D1–D4	4.5	Head	
	E	132.0	Main	
	C, D, D5, D6	14.0	Tail	
4	F1, F2, F3	17.0	Head	
	F4	8.0	Head	50.949
	G	77.5	Main	
	F5	7.5	Tail	50.955
	F6	7.0	Tail	50.952
	E, F, F7, F8	15.0	Tail	
5	G1	8.0	Head	50.936
	G2	8.0		50.950
	G3	9.0		50.938
	G4	8.5		50.950
	H	4.5		
	G5	6.5		50.941
	G6	7.5		
	G7	8.0		50.947
	G8	7.5	↓	50.951
	G	10.0	Tail	

The samples included in Table I were all condensed with carbon dioxide–alcohol mixtures; liquid air was used in some of the earlier distillations. The temperature of the paraffin oil-bath used in distilling the material was adjusted to maintain proper refluxing in the Hempel column. This temperature, which was about 120° in the first distillation, dropped abruptly to about 50° in the third distillation, and remained the same in the final distillations. The sudden fall was quite marked, and may be taken to indicate the removal of the last traces of chlorine and air. The amounts of chlorine and air present in even the first and second distillations, however, must have been quite small, since we experienced no difficulty in condensing samples in these distillations. As further evidence of the complete removal of air from the material, we may mention that the hydrolysis of the contents of the systems remaining after the second, third and fourth distillations gave only negligible amounts of residual gas.

One further observation bearing upon the purification of vanadyl trichloride may be noted here. The original preparation, containing mercury and excess chlorine, was frequently exposed to bright sunlight over a period of four months, and showed no marked changes. However, during the second distillation, when, judging from the above indications, most of the excess chlorine had been removed, a faint red discoloration appeared on the glass walls of the distillation apparatus. That this effect resulted from the action of light was demonstrated by the fact that sample **D3,** on exposure to sunlight, darkened markedly, and on long exposure became quite brown. Accordingly, we took precautions to guard our pure material against photochemical decomposition and carried out the two final distillations and the weighings of the sample bulbs in very dim yellow light.

The Analyses

The vanadyl trichloride samples for analysis were contained in sealed glass bulbs having a capacity of about 5 cc. The vanadyl trichloride was hydrolyzed, and titrated against silver nephelometrically. Standard methods,[7] adapted from various representative atomic weight determinations, were employed in the analyses. Only the details which indicate our adaptation of the standard procedures are described below.

Weighings.—A No. 10 Troemner balance, sensitive to about 0.02 mg. with a load of 50 g., was used for the weighings. The weights, which were of the best grade of lacquered brass, were calibrated just before, during and after use in this work. None of the weights used in the analyses showed any changes greater than 0.01 mg. except one 2.0-g. weight, for which it was necessary to increase the correction by 0.05 mg., in all of the gravimetric analyses. Weighings were made by the method of substitution, with precautions to avoid errors greater than 0.02 mg. Suitable counterpoises were used whenever possible. In the analysis of the "G" samples weighings were made in duplicate.

Vacuum corrections were calculated from the usual formula,[8] the air density being determined for every weighing by measurement of the temperature, pressure and relative humidity. Calibrated instruments were used.

The densities used in calculating the vacuum corrections were: silver, 10.5; silver chloride, 5.56; glass, 2.48; sodium chloride, 2.16; brass, 8.4.

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[7] See, for example, Richards and Wells, THIS JOURNAL, 27, 502 (1905); Briscoe and Little, J. Chem. *Soc.*, 105, 1327 (1914); Baxter and Scott, *Proc.* Am. *Acad. Arts Sci.*, 59, 33 (1923).

[8] Landolt-Börnstein's "Tabellen," 2d ed., p. 15.

Hydrolysis of the Vanadyl **Trichloride.**—Each sample bulb was broken in 500 cc. of solution in a heavy-walled two-liter pyrex Erlenmeyer flask, cooled in ice to 0°. For half of the samples, selected alternately from the distillation series, the solution contained 30 cc. of 15.6 M nitric acid. For the other samples, the solution was approximately **0.3** M ammonium hydroxide, freshly prepared by distilling concentrated aqua ammonia (sp. gr. 0.90) into water, in an all-glass apparatus.

After the bulb was broken, the flask was cooled for at least eight hours, opened, closed and cooled for another four hours, before the solution was filtered.

Separation and Collection of the Glass Fragments.—The solutions from the hydrolysis were filtered into glass-stoppered 3-liter pyrex Erlenmeyer flasks or 4-liter pyrex bottles, as follows. (a) The clear yellow liquid from the hydrolysis in acid was decanted through a low-ash[9] filter. The glass fragments of the bulb and the filter were washed with 500 cc. of water containing 20 cc. of 15.6 M nitric acid, in 50-cc. portions. (b) The ammoniacal liquid from the hydrolysis in alkaline solution was decanted through a low-ash filter. The precipitate in the flask was washed twice to remove most of the chloride, and dissolved in 60 cc. of 7.8 M nitric acid. The solution was poured through the filter. The glass fragments of the bulb and the filter were then washed with 500 cc. of water containing 20 cc. of 15.6 M nitric acid. In each case the final volume of the solution before precipitation was 1100 cc.

The glass fragments of the bulb were collected in the manner which we have previously described.[10]

Precipitation of Silver Chloride.—The solutions were precipitated with almost the theoretical amount of silver, weighed out and made up to 750 cc. in a solution containing 50 cc. of 15.6 M nitric acid. The partially diluted solution of silver nitrate was warmed to remove nitrous acid.

The silver solution was added to the chloride solution at the rate of about 4 cc. a minute. The final volume was in each case made up to 2250 cc. Subsequent titration showed the acid concentration to be 0.57 to 0.59 M in the solutions containing ammonium ion, and 0.65 M in the solutions containing no ammonium ion.

Determination of the End-Point.—After precipitation of the silver chloride, the stoppered flasks were first cautiously shaken by rotation, then violently shaken twice each day for twelve days. Two or three tests of the supernatant liquid from each analysis were made at this time. After four months another series of tests was made. The changes taking place

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[9] Ten weighings of the ash of thoroughly washed individual filters gave values varying from 0.01 to 0.07 mg. In the correction for the ash there is thus an uncertainty of about 0.03 mg.

[10] Scott and Johnson, J. Phys. *Chem.*, **33,** 1980 **(1929).**

during the interval were negligible. The maximum change in the average nephelometric ratio for any analysis was 0.09 units, which corresponds to —0.00010 g. of silver in the total volume of solution. At the completion of these tests the solutions were adjusted to the final end-point.

The procedure used in the above-mentioned tests and in the determination of the end-point was the same as that which we have previously described,[11] with this deviation: the 1-cc. portions of silver nitrate and sodium chloride standard solutions were added to the 20-cc. samples of the supernatant liquid, with identical stirring; the nephelometric observations took place between thirty and sixty minutes later.

The actual adjustment to the final end-point was continued until three independent series of 20 readings each, made over a period of a week, gave an average value within 0.05 unit of 1.00 for the ratio of the exposed lengths of the nephelometer tubes. The average deviation of the mean of each series from the final mean was about 0.02 unit. In most cases the end-point was "crossed.') The correction to make the ratio 1.00 exactly, which was never more than 0.06 mg., was calculated and is included in the value for the total silver added or subtracted in solution, in Table II.

In order to check the standard solutions employed, and the nephelometric procedure, nine saturated solutions of pure silver chloride containing varying amounts of nitric acid were tested at various times during the nephelometric observations. The average value found for the ratio of the exposed lengths of the tubes was 1.01, with an average deviation of 0.03 unit, the individual values varying from 0.94 to 1.05.

The analytical reagents used in this investigation were carefully purified, by methods[12] which we have previously outlined. Only one preparation of silver was used in the analyses. In the analysis of samples G1 to G8, inclusive, 20-cc. portions of liquids covering all of the ammonia, nitric acid and water added to the analytical solutions were tested nephelometrically for silver and chlorine. Only when the concentration of chloride was between the concentration of silver and the concentration of chloride in a solution containing sodium chloride equivalent to 0.02 mg. of silver per liter, was the liquid used in the analysis.

Results

Table II gives the results of all of the nephelometric analyses. The supernatant liquid from the analysis of sample G6, when first tested, showed a large excess of silver. The analysis was completed gravimetrically, giving the value 51.63 for the atomic weight of vanadium. This result is evidently due to some error, which a careful examination has failed to reveal.

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[11] Scott and Johnson, *J. Phys. Chem.*, **33,** 1981 (1929).

[12] Scott and Johnson, *ibid.*, **33,** 1978 (1929).

TABLE II

ATOMIC WEIGHT OF VANADIUM. $VOCl_3$:3Ag

Ag = 107.880; Cl = 35.457; O = 16.000

Sample of $VOCl_3$	$VOCl_3$ in vacuum, g.	Ag in vacuum, g.	Ag added or subtracted in soln., g.	Corr. wt. of Ag in vacuum, g.	Ratio $VOCl_3$:3Ag	Atomic weight of vanadium
F4	7 75120	14.47351	+0 00033	14.47384	0 535532	50.949
F5	7 62984	14 24619	+ ,00047	14 24666	.535553	50.955
F6	7 01143	13 09200	+ .00018	13 09218	.535543	50.952
G1	7 88453	14.72254	+ .00132	14.72386	.535493	50.936
G2	8 15697	15 23166	− .00023	15.23143	.535535	50.950
G3	9 19783	17.17479	+ ,00135	17.17614	.535500	50.938
G4	8 29538	15.48965	+ .00021	15.48986	.535536	50.950
G5	6 69572	12 50289	+ .00055	12.50344	.535510	50.941
G7	8 04970	15 03074	+ .00062	15 03136	.535527	50.947
G8	7.60527	14.20116	− .00005	14.20111	.535541	50.951
				Mean	.535527	50.947

The values of the atomic weight from Table II are arranged below according to the decreasing volatility of the samples, and the nature of the solutions used in their hydrolysis.

Ammoniacal hydrolysis		Acid hydrolysis	
Sample	Atomic weight $VOCl_3$:3Ag	Sample	Atomic weight $VOCl_3$:3Ag
F4	50.949	G2	50.950
G1	50.936	G4	50.950
G3	50.938	G8	50.951
G5	50.941	F6	50.952
G7	50.947		
F5	50.955		
Mean	50.945		50.951
Average deviation	0.006		0.001

There is no trend in the "acid" series. In the "ammonia" series the values of the atomic weight, with one exception, are lower than the values in the "acid" series, and show a regular increase with decreasing volatility of the samples, particularly apparent in the fractions from the last distillation.

Two observations which were made at the conclusion of the fourth distillation seemed to establish the uniformity of our material at this stage of the purification. Analysis of more and less volatile samples gave essentially the same values for the atomic weight. The hydrolysis of the residual vapor in the apparatus from the fourth distillation, carried out soon after the completion of the distillation, yielded only a negligible amount of residual gas.

Subsequent observations, however, suggest that the variations noted above were caused by the presence of chlorine in the samples. A faint chlorine-like odor was detected during the filtration of the solutions from the "acid" hydrolysis of samples G2, G4, G6 and G8. The hydrolysis of the material remaining in the 400-cc. all-glass system from the fifth distillation gave about 3 cc. of residual gas, mostly chlorine. This system contained 10 g. of the extreme tail fraction of the vanadyl trichloride, which had been standing for five months in a dark cupboard. It showed no discoloration which would indicate a leak.

It may be noted that if chlorine were present in the samples as an impurity, it would tend to make the mean value 50.945 derived from the "ammonia" series too low, and the value 50.951 from the "acid" series a little too high. Under the circumstances, the close agreement between the mean values of the atomic weight derived from the "acid" and "ammonia" series, and the small range, 0.019 unit, covered by the entire nephelometric series, shows that only extremely small amounts of chlorine could have been present. Since chlorine is the only impurity whose presence there is any occasion to suspect, it seems reasonable to conclude that the atomic weight of vanadium lies between the above limits, and cannot be far from the mean value, 50.947, obtained from all of the nephelometric analyses.

As a means of confirming this conclusion, we have extended the experiments to take into account two possible sources of constant error in the analytical method. If the coagulating actions of equivalent amounts of silver nitrate and sodium chloride, added in excess according to the usual procedure, are not equally affected by the presence of vanadic acid, the nephelometric end-point may not corrrespond to the stoichiometrical point. To investigate this possibility, the supernatant liquids from the analyses of the "G" samples, after adjustment to the end-point, were analyzed for their silver and chloride content. The measurements were made in the usual way by direct nephelometric comparison against standard silver and chloride solutions. In these comparisons, in order to eliminate any disturbing action of the vanadic acid, the same precipitating ions were present in excess (in equal amounts) in the "standard" and "unknown" tubes, and the concentrations of vanadic acid, ammonium ion and nitric acid in the two tubes did not differ by more than 1%. Similar measurements were also made upon four saturated solutions of silver chloride in 0.65 M nitric acid.

In these experiments two effects were found which may be attributed to the presence of vanadic acid. Every one of the supernatant liquids from the seven analyses contained more silver than chloride ion. The (approximate) "solubility product" of silver chloride was greater in the analytical solutions than in the saturated solutions of silver chloride. It may be noted that the observed deviations are only a little greater than the analytical error. Thus, on the assumption that the excess of silver found in each solution is real, the mean atomic weight calculated[13] from the seven ex-

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[13] When the apparent excess of silver is taken into account the average $VOCl_3$:3Ag ratio from the seven analyses is 0.535536 ± 0.000011.

periments is **50.950** instead of **50.945.** While the results of these experiments can obviously be regarded only as provisional, they indicate that any error due to the effect of vanadic acid on the nephelometric end-point is small.

The possibility of a serious error due to the contamination of the precipitate has also been investigated. In three analyses from each of the "acid" and "ammonia" series the precipitated silver chloride was collected and weighed. The usual gravimetric procedures[14] were followed in collecting the silver chloride and in determining the silver chloride in the wash liquors. The results of these gravimetric analyses are given in Table III.

TABLE III

SUMMARY OF RESULTS. $VOCl_3:3AgCl$

Sample of $VOCl_3$	AgCl in vacuum, g.	Loss on fusion, g.	AgCl removed in supernatant liquid, g.	AgCl dissolved in washings, g.	Corr. wt of AgCl in vacuum, g.	$VOCl_3:3AgCl$ Ratio	Atomic weight of vanadium
G1	19 55896	0.00035	0.00220	0.00137	19 56218	0.403050	50.945
G2	20 23316	.00041	.00117	.00127	20 23483[a]	,403115	50 973
G3	22 81668	.00037	,00214	,00079	22 81924	,403073	50.955
G4	20 57677	,00021	,00140	,00076	20 57872	,403105	50.969
G7	19 96741	.00031	.00183	,00083	19 96976	,403094	50.964
G8	18.86606	.00031	.00136	,00059	18.86755"	.403087	50.961
					Mean	.403087 ±0.000006	50.961

[a] Corrected for total chloride added in the nephelometric analysis.

The loss on fusion of the silver chloride is the value found after an initial heating of about sixteen hours in an electric furnace at 300°. Part of the data for the estimation of the chloride removed in test portions of the supernatant liquid was obtained in the experiments described above; another part, in additional experiments of the same nature.

The many tests made upon the supernatant liquids limit to a considerable extent the precision of the gravimetric analyses. Nevertheless, the results of these analyses do show that there is no serious contamination of the precipitated silver chloride. In fact, the mean value **1.32855 ± 0.000012** for the AgCl:Ag ratio calculated for the six analyses completed gravimetrically, is low rather than too high. Further evidence of the absence of coprecipitation of vanadium is the fact that the fused silver chloride was always white. One milligram of vanadic oxide in twenty grams of fused silver chloride gives a distinct color to the mixture.

We are indebted to the Vanadium Corporation of America for the gift of the vanadic oxide used in this work.

Summary

The analysis of vanadyl trichloride has yielded for the $VOCl_3:3Ag$ ratio

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[14] See, for example, Baxter and Moore, THIS JOURNAL, 34, 1651 (1912).

the value 0.535527 ± 0.000004, from which the atomic weight of vanadium is found to be 50.947.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

ELECTRICAL CONDUCTANCE OF COBALT SULFATE SOLUTIONS[1]

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This paper records the results of an investigation of the conductances of cobalt sulfate solutions, and is the first of a series dealing with the properties of solutions of cobalt salts.

The conductivities of cobalt sulfate solutions have been determined previously by Jones and Jacobson[2] for concentrations varying between N and *N*/1024 at 0, 10, 25 and 35°. This was part of an investigation of the influence of temperature upon the dissociation of thirty-four electrolytes. For reasons to be discussed later, we felt that it was necessary to repeat the measurements of the conductances of cobalt sulfate solutions.

Materials

Conductivity Water.—The conductivity water was prepared by the usual method of redistilling distilled water with alkaline potassium permanganate and condensing the vapor in a block-tin condenser. The water was kept in a six-liter pyrex flask fitted with a siphon and a soda lime tube. All the water used had a conductivity between 1.2 $\times 10^{-6}$ and 2.0 $\times 10^{-6}$ mhos.

Cobalt Sulfate.—Chloropurpureocobalt chloride $[Co(NH_3)_5Cl]Cl_2$ was prepared by the method of Sørensen[3] and was converted to the carbonate and eventually to the sulfate. The cobalt sulfate was precipitated by means of absolute alcohol, and was then twice recrystallized from conductivity water.

Cobalt Sulfate Solutions.—A solution of cobalt sulfate, approximately 0.5 N, was prepared and this was standardized by an electrolytic determination of its cobalt content. The exact amount of conductivity water needed to make the solution exactly 0.5 N was added from a calibrated buret, and from this stock solution was prepared the 0.2 *N* by diluting 100 cc. of the 0.5 N to a volume of 250 cc. Similarly the 0.1 N solution was prepared by diluting 100 cc. of the 0.5 N to 500 cc. The third "standard" solution 0.05 N was prepared in a similar manner.

In this way three solutions were prepared from the 0.5 N solution. Also duplicate solutions were made by dilution in different ratio, for example, the 0.1 N from the 0.2 N, etc.

The above method was followed for the preparation of the more dilute solutions. In every case at least 100 cc. of a "standard" solution was used in the dilution.

Experimental Method

The conductivity was measured by the Kohlrausch bridge method using two Washburn cells,[4] Types A and B. A new Leeds and Northrup Stu-

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[1] This paper is an abstract of a part of the doctorate thesis of Alfred J. Berger.

[2] H. C. Jones and C. A. Jacobson, *Am.* Chem. **J., 40, 355** (1908).

[3] Sørensen, Z. anorg. *Chem.*, 5, 369 (1894).

[4] Washburn, THIS JOURNAL, 38, 2449 (1916).

dent's Potentiometer was used as the slide wire, and dial resistances were supplemented when necessary by calibrated plug resistances. Plug resistances were used for only three of our measurements, namely, 0.002 N, 0.001 N and in the determination of cell constant of Cell A. Jones and Josephs[5] show that the error due to use of plug resistances not designed for use with alternating current amounts to –0.012% at 1100 cycles for a resistance of 5000 ohms.

The alternating current was furnished by a Leeds and Northrup microphone hummer which maintained a sufficiently pure sine wave of 1000 cycles.[6] Location of the null point was simplified by use of a one-step audio-amplifier of conventional radio design.[7] The capacity necessary to balance that of Cell A was determined by a large calibrated radio condenser, and this capacity was obtained by means of a 0.00075-microfarad fixed condenser shunted with a conventional thirteen-plate variable condenser. This assured a good minimum in the phones at all times (see Fig. 1).

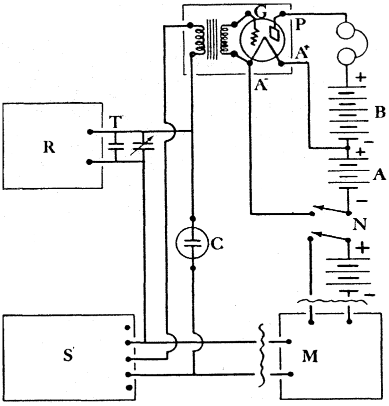

Fig. 1.—Arrangement of apparatus for conductivity measurements. C, Conductivity cell; M, microphone hummer; N, double pole switch; R, resistances; S, student type potentiometer; T, 0.00075 mf.

The cell constant of Cell B was determined with a 0.01 N solution of potassium chloride (twice recrystallized from conductivity water). The potassium chloride solutions were prepared according to the weight method of Kraus and Parker[8] and also according to the volume method of Randall.[9] The cell constants obtained by the use of solutions made by the two methods agreed within 0.05% and the average 0.80373 was taken as the cell constant of Cell B. Bray and Hunt's[10] value for the conductivity of 0.01 N potassium chloride, corrected according to Randall,[11] namely, 0.0014120 mhos, was used in the calculations.

The cell constant of Cell A was obtained by the use of solutions, approximately 0.0005 N, the specific conductivities of which were determined by the use of Cell B, and these values were then used in the calculations of the

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[5] G. Jones and R. C. Josephs, THIS JOURNAL, **50**, 1081 (1928).

[6] "Experimental Physical Chemistry," by Daniels, Mathews and Williams, McGraw-Hill Book Co. Inc., New York, 1929, p. 387.

[7] Hall and Adams, THIS JOURNAL, **41**, 1515 (1919).

[8] Kraus and Parker, *ibid.*, **44**, 2422 (1922).

[9] Randall, *ibid.*, **49**, 1488 (1927).

[10] Bray and Hunt, *ibid.*, **33**, 781 (1911).

[11] Randall and Scalione, *ibid.*, **49**, 1486 (1927).

constant for Cell A.[12] The average value for the cell constant using five different solutions was 0.023206.

Cell B was used between the normalities 0.5 and 0.001 N, and Cell A between 0.0005 and 0.0001 N. The conductivities of the solutions were measured at 25.00 ± 0.01°.

Results

Table I contains the averages of the specific conductances thus obtained and the equivalent conductances calculated from them. For purposes of comparison the corresponding values for nickel sulfate solutions, as determined by Murata,[13] are also included.

TABLE I

CONDUCTANCE OF COBALT SULFATE SOLUTION AT 25°

Concn., N	Specific conductance	Equivalent conductance	$NiSO_4$ (Murata)
1.0	....	.....	29.091
0.5	17718×10^{-6}	35.436	35.222
.2	8778×10^{-6}	43.890	43.585
.1	5111.8×10^{-6}	51.118	50.755
.05	2978.8×10^{-6}	59.576	59.160
.02	$1448\ 2 \times 10^{-6}$	72.410	72.254
.01	827.78×10^{-6}	82.778	82.69
.005	466.2×10^{-6}	93.24	93.16
.002	210.0×10^{-6}	105.0	105.49
.001	112.7×10^{-6}	112.7	113.05
.0005	59.35×10^{-6}	118.7	118.66
.0002	24.74×10^{-6}	123.7	124.14
.0001	$12\ 39 \times 10^{-6}$	123.9	126.90

Discussion of Results

Ostwald's dilution equation, as deduced from the law of mass action, is as follows: $(C\alpha)^2 = KC(1 - \alpha)$ where $\alpha = \Lambda/\Lambda_0$. Λ is the equivalent conductance of a solution of a given concentration, Λ_0 is the equivalent conductance of a solution of zero concentration. The above equation may be simplified, giving the expression

$$\Lambda = \Lambda_0 - \frac{\Lambda^2 C}{K\Lambda_0} \tag{1}$$

If we write Equation 1 in the more general form corresponding to Storch's Equation,[14] we get

$$\Lambda = \Lambda_0 - \frac{\Lambda^n C^{n-1}}{K\Lambda_0^{n-1}} \tag{2}$$

as $\Lambda \longrightarrow \Lambda_0$, this becomes

$$\Lambda \simeq \Lambda_0 - \frac{\Lambda_0 C^{n-1}}{K} \tag{3}$$

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[12] *See* Weiland, THIS JOURNAL, **40,** 136 (1918).

[13] *Murata, Bull. Chem. Soc. Japan,* **3,** 47 (1928).

[14] Storch, *Z. physik. Chem.,* 19, 13 (1896).

Equation 3 suggests the origin of equations of the form

$$\Lambda = \Lambda_0 - BC^{n-1} \tag{4}$$

Several equations have been proposed of this form. Kohlrausch[15] gives $\Lambda = \Lambda_0 - BC^m$, where $m = 1/3$ or $m = 1/2$. Lorenz[16] and Walden[17] suggest that $m = 0.45$. Debye and Hückel[18] deduce an equation of this form, and show that m should have the value $1/2$, this value being independent of the nature of the electrolyte.

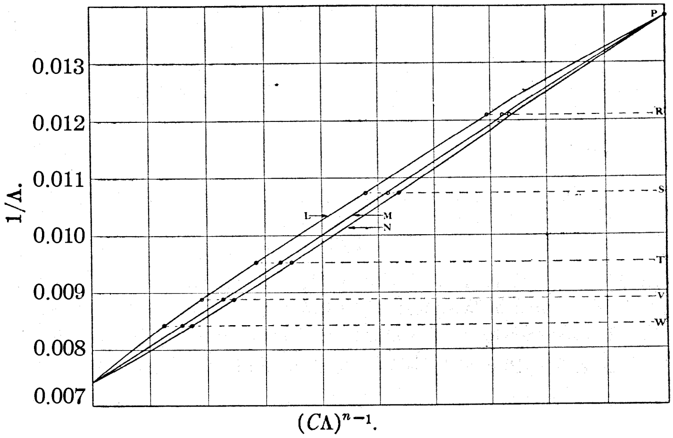
To evaluate n in Equation 2 we have employed the graphic method of A. A. Noyes.[19] Equation 2 is equivalent evidently to

$$\frac{1}{\Lambda_0} = \frac{1}{\Lambda} - \frac{\Lambda^{n-1}C^{n-1}}{K\Lambda_0^n} \tag{5}$$

or

$$\frac{1}{\Lambda_0} = \frac{1}{\Lambda} - K'(C\Lambda)^{n-1} \tag{6}$$

Accordingly, in Fig. 2, the values of $(C\Lambda)^{n-1}$ in the range from 0.0005 to 0.02 N have been plotted as abscissas against the values of $1/\Lambda$ as ordinates, by varying the value of $n - 1$ until a plot as linear as possible was obtained. In this plot we have not included the values for 0.0002 and 0.0001 N, as these are evidently in much greater error than are our other determinations. The value of Λ_0 was obtained graphically by extrapolation of the plotted



L, $n = 1.85$; M, $n = 1.58$; N, $n = 1.55$. P, 0.02 N; R, 0.01 N; S, 0.005 N; T, 0.002 N; V, 0.001 N; W, 0.0005 N.

Fig. 2.—Plot of Storch's function.

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[15] Kohlrausch, "Das Leitvermögen der Elektrolyte," 1916, p. 107.

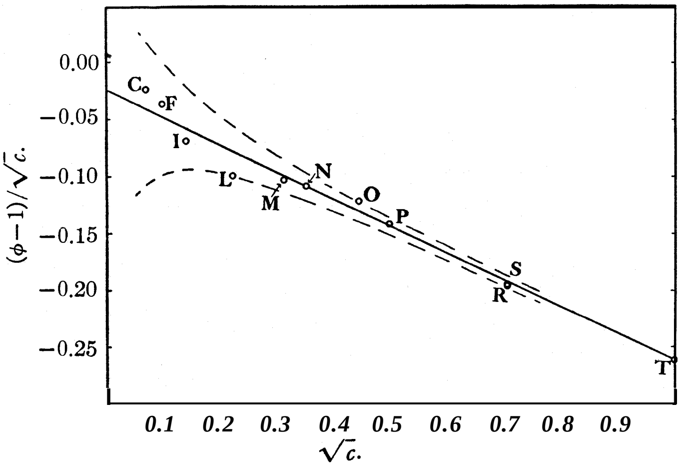
[16] Lorenz, *Z. anorg. Chem.*, 108,191 (1919).

[17] Walden, *ibid.*, **115**, 49 (1921).

[18] Debye and Hückel, *Z. Physik*, 24,305 (1923).

[19] Noyes and Johnston, THIS JOURNAL, 31, 987 (1909); Noyes and Falk, *ibid.*, 34, 454 (1912).

line to zero concentration where $C\Lambda = 0$. In Fig. 2, in order to make the various curves comparable, the value of $(C\Lambda)^{n-1}$ for the highest concentration (0.02 N) was made 100 for each value of n, and the other values were proportionally varied. The value of the exponent for cobalt sulfate at 25° was found to be 1.58, and the value for Λ_0 was found to be 134.6 mhos at this temperature. It is interesting to note that Murata[13] found the exponent $n = 1.60$, for nickel sulfate at 18 and 25°. According to Noyes and Falk,[19] for all bi-bivalent sulfates n takes a value not far from 1.6 for the concentration interval 0.0001 to 0.02 N. Noyes also points out that the variation of n with the temperature is negligible.



C, 0.005 *N;* F, 0.01 *N;* I, 0.2 *N;* L, 0.5 *N;* M, 0.1 *N;* O, 0.2 *N;* *R*, *0.5 N.* **Data of Wagner: N,** ***0.125 N; P, 0.25 N;*** **S,** ***0.5 N;*** **T,** ***1 N.*** **Upper curve,** ***0.5%*** **deviation; lower curve,** ***0.5%*** **deviation.**

Fig. 3.—Plot of $(\phi - 1)/\sqrt{c}$ for cobalt sulfate at 25°.

We have attempted to apply the Noyes method to Jones and Jacobson's results,[2] that is, we have plotted $1/\Lambda$ against $(C\Lambda)^{n-1}$ for values of $n = 1.58$, $n = 1.50$, $n = 1.40$. The plot for $n = 1.40$ was nearest to a straight line. At C = 0, the corresponding l/A value gave $\Lambda_0 = 154$. However, their points do not fall closely upon a straight line and their final A value is 107.05. Hence, such a large extrapolation is not likely to be accurate. Again, the value of n necessary *to* make the plot approximate a straight line is not in agreement with Noyes' observation that the value for n for most bi-bivalent salts lies close to 1.60.

The Relative Viscosities of Cobalt Sulfate Solutions.—The measurements of relative viscosities were made with an Ostwald viscosimeter in the usual manner. Wagner[20] determined the relative viscosities of cobalt sulfate solutions for concentrations N, $N/2$, $N/4$, $N/8$ at 25°. As a matter

[20] **Wagner, Z.** ***physik. Chem., 5, 31 (1890).***

of interest, we have plotted the Jones and Dole[21] function $(\phi - 1)/\sqrt{c}$ against $\sqrt{c}$ for our values, and have included Wagner's viscosity values on the graph. The resulting curve should be a straight line (see Fig. 3). The maximum deviation of our measurements—for 0.2 N—is 0.56% from that required by the straight line relation. The greatest deviation in Wagner's data—for 0.5 N—is 0.23%. The nature of the plot is such as to magnify the apparent percentage of deviation at the low concentrations.

We have used the viscosity ratio as an approximate correction for the mobiiity term $[(U_{C^+})_0 + (U_{A^-})_0]/U_{C^+} + U_{A^-}$ in the equation[22]

$$\gamma = \frac{\Lambda}{\Lambda_0}\,\frac{(U_{C^+})_0 + (U_{A^-})_0}{U_{C^+} + U_{A^-}}$$

The measurements of the relative viscosities and the conductance–viscosity ratios are given in Table II.

TABLE II

CONDUCTANCE–VISCOSITY RATIOS OF COBALT SULFATE SOLUTIONS

Normality	d^{25}_{25}	$\frac{\Lambda}{\Lambda_0}$	$\frac{\eta}{\eta_0}$	$\frac{\Lambda}{\Lambda_0} \times \frac{\eta}{\eta_0}$
0.5	1.0380	0.26327	1.1613	0.30574
.2	1.0158	.32608	1.0579	.34496
.1	1.0079	,37978	1.0337	.39258
.05	1.0040	.44262	1.0230	,45280
.02	1.0020	,53797	1.0099	.54330
.01	1.0009	.61499	1.0035	.61714
.005	1.0004	,69272	1.0017	.69390
.002	1.0000	.78009	1.0000	.78009
.001	1	.83730	1.0000	.83730
.0005	1	.88187	1	.88187
.0002	1	.91902	1	.91902
.0001	1	.92051	1	.92051

In a later paper we hope to compare these conductance–viscosity ratios with the activity coefficients of the same solutions.

Summary

The conductance of aqueous cobalt sulfate solutions at concentrations 0.0001 to 0.5 N has been measured at 25°.

The exponent n in the equation

$$\Lambda = \Lambda_0 - \frac{\Lambda^n C^{n-1}}{K\Lambda_0^{n-1}}$$

was found to be equal to 1.58 for cobalt sulfate, and Λ_0 by extrapolation by means of this equation was found to be 134.6 mhos.

The relative viscosities of the above solutions have been determined and the conductance–viscosity ratios have been calculated.

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[21] Jones and Dole, THIS JOURNAL, 51, 2950 (1929).

[22] Noyes and Sherrill, "Chemical Principles," Macmillan Co., New York, 1923, p. 117.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE VAPOR PRESSURE AND VAPOR DENSITY OF SODIUM

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Some years ago Rodebush and DeVries[1] published the results of measurements of the vapor pressure of sodium at very low pressures by the effusion method of Knudsen. In this paper they reviewed previous work. The only previous measurements that appeared good were those of Haber and Zisch[2] in the pressure range 2–12 mm. Their measurements were made by a dynamic method. Edmondson and Egerton[3] have repeated and confirmed the work of Rodebush and DeVries. No satisfactory measurements are to be found in the literature for higher pressures except some not very recent determinations of the boiling points.[4] It seems doubtful whether a boiling point can be determined at high temperatures with a satisfactory degree of accuracy.

There is plenty of evidence in the literature that the vapor of sodium is monatomic. Robitsch[5] determined the velocity of sound in the vapor at the boiling point and calculated the ratio of specific heats to be 1.68. Taylor[6] found no evidence of molecules in the saturated vapor at pressures of 10^{-2} mm. When the vapor pressure data of Rodebush and DeVries, Edmondson and Egerton and Haber and Zisch are plotted together with the boiling points as found in the literature on a log p–$1/T$ diagram, the points all fall very close to a straight line. Since these vapor pressures obtained by both the effusion and the dynamic methods involve the assumption of normal vapor density,[7] the excellent agreement of the results by the different methods seems to argue for a normal vapor density. Rodebush[8] used these data to calculate the entropy of the sodium atom in the vapor state and obtained excellent agreement with the theory for an atom in a ^2S ground state.

However, the straight line obtained in the vapor pressure plot previously mentioned does not agree with the value of C_p of $5/2R$ to be expected for a monatomic vapor. With the discovery of a band spectrum due to diatomic molecules in the vapors of the alkali metals, it was established that these vapors could not longer be considered strictly monatomic.

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[1] Rodebush and DeVries, THIS JOURNAL, 47, 2488 (1925).

[2] Haber and Zisch, *Z. Physik*, 9, 325 (1922).

[3] Edmondson and Egerton, *Proc. Roy. Soc.* (London), **A113,** 520 (1927).

[4] Heycock and Lamplough, *Proc. Chem. Soc.*, 28, **3** (1912).

[5] Robitsch, *Ann. Physik*, 38, 1027 (1912).

[6] Taylor, *Phys. Rev.*, 28, 576 (1926).

[7] The pressure calculated by the dynamic method varies inversely as the assumed vapor density, while for the effusion method the relation is more involved.

[8] Rodebush, *Proc. Nat. Acad. Sci.*, **13,** 185 (1927).

In the case of potassium, Carelli and Pringsheim[9] showed that the association was small, but in the case of sodium Loomis[10] calculated the heat of dissociation to be 1.0 ± 0.1 volt and thermodynamic calculations[11] have been made which predict that there will be more molecules than atoms in sodium vapor at the boiling point. In view of the conflicting evidence it seemed desirable to determine accurately the amount of association in saturated sodium vapor.

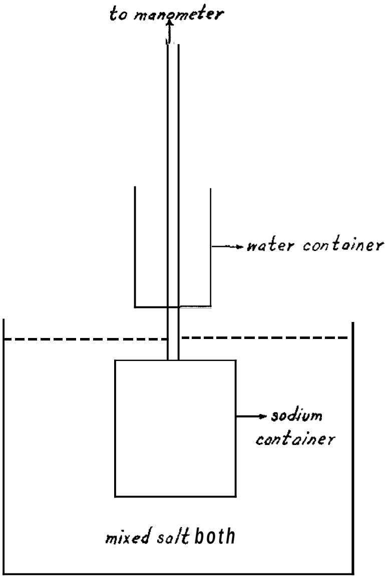
Method

Since the only material suitable as a container for sodium at high temperatures is pure nickel, it was impossible to use the ordinary methods of measuring vapor pressure. The method used involves a simple application of Dalton's law of partial pressures. The sodium was vaporized in a large container in the presence of argon. The container was connected by a narrow tube to a mercury manometer. The sodium vapor which diffused up the tube was condensed and refluxed back into the container. When a static condition was established, the external pressure of argon was equal to the combined pressure of sodium and argon in the container. From the known volumes and the quantity of argon in the apparatus the pressure of the sodium can be calculated.

The vapor density was measured by determining the amount of sodium vaporized when a measured quantity of argon was passed over metallic sodium.

Apparatus

A. Vapor Pressures.—In general the vapor pressure apparatus consisted of a mercury manometer connected to a nickel bomb in which the sodium was heated. A diagram of the nickel bomb is given in Fig. **1.** The bomb was constructed by welding a nickel tube about **30** cm. long and **0.5** cm. in internal diameter to a cylindrical nickel container **10** cm. high and having a 7-cm. base. In order that sodium vapor would not distil into the manometer system, a cylindrical copper water jacket 7 cm. long was soldered to the nickel tube **8** cm. above the top of the nickel container. This copper jacket, filled with boiling water in order to prevent the solidification of the sodium, served as a condenser to reflux the sodium back into the bomb. The nickel tube and



Pig. 1.

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[9] Carelli and Pringsheim, *Z. Physik*, 44, **643 (1927).**

[10] Loomis, *Phys. Rev.*, 31, **323 (1928).**

[11] Harrison and Slater, *ibid.*, 26, **176 (1925);** Villars, *Proc. Nat. Acad. Sci.*, *14*, **508 (1928).**

pyrex manometer were connected by means of a picein seal. A water-jacketed condenser placed between the picein seal and the copper jacket prevented the picein from melting.

Two stopcocks were sealed into the arm of the manometer connected to the nickel bomb, in order that the system might be evacuated and argon admitted. The argon was passed from a gas measuring buret through a constricted capillary which permitted as small amounts of argon as desired to be admitted into the system.

By the use of a leveling bulb, the mercury in the arm of the manometer connected to the nickel bomb was maintained at a constant level in order that the volume above this level would remain constant. The other arm of the manometer was evacuated with a Cenco Hyvac pump in order to make the manometer of the absolute type.

The bomb was immersed in a mixed salt bath of equal parts by weight of sodium chloride and potassium carbonate (m. p. 560°), which was held in an electric furnace with a cylindrical iron core. A uniform temperature was maintained throughout the bath by means of a mechanical stirrer. Temperature control was obtained by varying the 220-volt alternating current through the furnace by means of a hand-controlled rheostat. All temperatures were measured with a platinum–platinum–rhodium thermocouple. The thermocouple, which was sheathed in quartz, was protected from the corrosive action of the salt bath by means of a close fitting iron tube, placed directly next to the bomb.

B. Vapor Densities.—Vapor densities were determined by a dynamic method, employing the apparatus shown in Fig. 2. F is an electric furnace with a cylindrical copper core. A and B are nickel tubes. One end of B was constricted to a small orifice O about 1.5 mm. in diameter. The other end of B was connected to a drying train consisting of a sulfuric acid bubbler, soda and lime, and phosphorus pentoxide drying tubes, through which argon was admitted from a cylinder. D is a nickel wire for inserting the nickel boat C into Tube B. The outlet of Tube A leads to a five-liter aspirator bottle containing water saturated with argon at atmospheric pressure. The rate of flow of the argon was regulated by the rate of removal of water from the aspirator bottle and the volume of argon passed was determined by measuring the volume of water removed. The system was connected to the atmosphere through a sulfuric acid bubbler and the pressure of argon was kept equal to that of the atmosphere by regulation of the automatic valve on the argon cylinder. The thermocouple is shown at T.

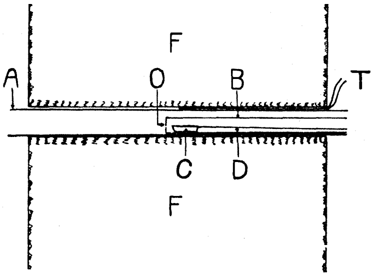

Fig. 2.

Method

A. Vapor Pressure.—The nickel bomb was first evacuated by means of a Cenco Hyvac pump and filled with argon. About 6 g. of sodium which had been put through a sodium press was inserted into the bomb, and the nickel tube sealed to the manometer. The system was evacuated for several hours at a temperature of 400 to 500° in order to remove all volatile impurities from the sodium. After this treatment, a measured amount of argon was admitted into the system through the capillary tube and the temperature of the bath regulated by means of a rheostat until a constant temperature had been maintained for thirty minutes or more. The temperatures of the bath, the cooling water and the room, and the total pressure in the system as indicated by the manometer, were recorded. The pressure readings of the manometer were read to 0.1 mm. by means of a cathetometer. The temperature of the bath was then raised to the next desired temperature and the readings recorded as before. This procedure was repeated until the vapor pressures of sodium up to the boiling point had been determined, argon being admitted into the system from time to time in order to keep the total pressure to approximately twice the vapor pressure of the sodium.

The vapor pressure of the sodium was calculated from the equation

$$P_{\mathrm{Na}} = P_{\mathrm{T}} + \frac{P_{\mathrm{T}}\left(\frac{V_2}{T_2} + \frac{V_3}{T_3} + \frac{V_4}{T_4}\right) - \frac{P_{\mathrm{A}}V_{\mathrm{A}}}{T_{\mathrm{A}}}}{V_1/T_1} \qquad (1)$$

in this formula P_{Na} is the vapor pressure of the sodium, P_{T} is the total pressure of the system as indicated by the manometer, V_2/T_2, V_3/T_3 and V_4/T_4 are the various volumes of the apparatus external to the bath divided by their corresponding temperatures, V_1 is the volume occupied by the sodium vapor at the temperature T_1, and P_{A}, V_{A} and T_{A} are the pressure, volume and temperature of the argon when admitted into the system.

This equation was derived from a simple consideration of the perfect gas law. If M_{A} moles of a gas are in an enclosed system whose total volume is divided into the several volumes V_1, V_2, ... V_n, which are subjected to the corresponding temperatures T_1, T_2, T_3 . . . . T_n, then

$$M_{\mathrm{A}} = \frac{P_{\mathrm{T}}}{R}\left[\frac{V_1}{T_1} + \frac{V_2}{T_2} + \dots + \frac{V_{\mathrm{n}}}{T_{\mathrm{n}}}\right] \qquad (2)$$

where P_{T} is the total pressure of the gas and R the gas constant. If V_1 be occupied by not only gas A but gas Na whose pressure is P_{Na}, then

$$M_{\mathrm{A}} = \frac{(P_{\mathrm{T}} - P_{\mathrm{Na}})}{R}\frac{V_1}{T_1} + \frac{P_{\mathrm{T}}}{R}\left[\frac{V_2}{T_2} + \dots \frac{V_{\mathrm{n}}}{T_{\mathrm{n}}}\right] \qquad (3)$$

If M were measured at a pressure P_{A}, V_{A} and T_{A}, then

$$M_{\mathrm{A}} = \frac{P_{\mathrm{A}}V_{\mathrm{A}}}{RT_{\mathrm{A}}} \qquad (4)$$

Substituting this value for M_{A} in Formula 3 and multiplying through by R, the gas constant, Equation 5

$$\frac{P_{\mathrm{A}}V_{\mathrm{A}}}{T_{\mathrm{A}}} = (P_{\mathrm{T}} - P_{\mathrm{Na}})\frac{V_1}{T_1} + P_{\mathrm{T}}\left(\frac{V_2}{T_2} \dots + \frac{V_{\mathrm{n}}}{T_{\mathrm{n}}}\right) \qquad (5)$$

is obtained, which when divided by V_1/T_1 and the terms rearranged, gives Equation 1. The volumes were determined by weighing the apparatus first empty and then filled with water, the difference in weight divided by the density of water at the temperature of the water, giving the volume. The total volume of the system was also checked in another manner. A bulb was blown in the manometer system and marks made above and below the bulb in such a manner as to make the capacity of the bulb exactly 55 cc. The system was then evacuated by means of a Cenco Hyvac pump and refilled with argon. With the system at atmospheric pressure, P_1, the mercury level in the manometer was then adjusted to the mark above the bulb. All stopcocks were then closed and the mercury level in the manometer adjusted to the mark below the bulb. When temperature equilibrium was obtained, the new pressure reading P_2 was observed, and the total volume of the apparatus, V_1, calculated from the equation, $P_1V_1 = P_2 (V_1-55)$. The volume of the bomb as obtained in this manner checked within a few tenths of a per cent. with the volume as obtained by weighing the bomb empty and filled with water. A final check on all volumes was also made when dismantling the apparatus; again the results were in good agreement with the volumes as determined above. At high temperatures allowance was made for the change in volume due to the expansion of the nickel bomb and the decreased density of sodium.[12]

The supply of dried argon was kept in a gas buret over mercury. The buret containing the argon was graduated to 0.05 cc. and estimation could be made to 0.01 cc. As no less than 10 cc. of argon was admitted into the system at one time, the error from this source should not exceed a few tenths of a per cent. The capacity of the buret was carefully checked in order that no volume error should enter from this source. Manometer readings were made with a cathetometer having an invar scale and were reproducible to 0.1 mm.

It is true that in deriving Equation 1 from which the vapor pressures were calculated, the assumption was made that the temperature boundaries, *i.* e., T_1, T_2, etc., were sharp and well defined. This assumption was justified, as the external volume, *i.* e., the volume not actually contained in the bath, was very small (less than 10%) compared to the total volume of the system. Hence, the error due to the temperature gradients is of little consequence.

B. Vapor Densities.—In making a vapor density determination, the entire vapor density apparatus was first filled with argon. The furnace was brought up to the proper temperature, and 1 to 2 g. of sodium, which had been previously put through the sodium press, was placed in the boat C and introduced into the tube B. Argon at a constant rate of flow was passed through tube B over boat C containing the sodium at the desired temperature. Saturated with sodium vapor, the argon passed through the small orifice O, and deposited the sodium in the cooler portion of the tubes A and B. A steady rate of flow of argon was maintained until from 2 to 2.5 liters had passed over in this manner. The moles of argon passed were calculated from the volume of water, after correcting for the vapor pressure of the water. At the end of the run the flow of argon was cut off, the furnace shut down, the boat removed from tube B and tubes A and B withdrawn. The amount of sodium which had deposited upon tubes A and B was determined by titration with 0.1 or 0.5 N hydrochloric acid solution as seemed best.

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[12] "International Critical Tables."

The vapor density of the sodium was calculated from the following equation

$$M_{\mathrm{Na}} = \frac{P_{\mathrm{T}}\,W_{\mathrm{Na}}}{P_{\mathrm{NA}}\,N_{\mathrm{a}}} - \frac{W_{\mathrm{Na}}}{N_{\mathrm{A}}} \qquad (6)$$

W_{Na} is the weight in grams of the sodium which saturated N_{A} moles of argon, P_{T} is the total pressure of the system, P_{Na} is the vapor pressure of the sodium at the temperature at which the vapor density run was carried out, and M_{Na} the molecular weight of the sodium. If gas Na and A occupy a system at a total pressure of P_{T}, the partial pressure of gas Na, P_{Na}, is equal to the total pressure times its mole fraction in the mixture or

$$P_{\mathrm{Na}} = P_{\mathrm{T}}\frac{\dfrac{W_{\mathrm{Na}}}{M_{\mathrm{Na}}}}{\dfrac{W_{\mathrm{Na}}}{M_{\mathrm{Na}}} + N_{\mathrm{A}}} \qquad (7)$$

Upon simplification of this equation, Equation 6 is obtained.

A. Materials, Analytical Methods, **Etc.**—In this work a commercial grade of sodium was used. Spectroscopic tests made on the sodium showed it to be free from lithium and potassium. The hydrochloric acid was standardized with a standard solution of sodium hydroxide. The sodium hydroxide was standardized with potassium acid phthalate, which was kindly furnished by Dr. L. W. Elder of this Laboratory. The normalities of the acid solutions were checked with sodium carbonate solutions. Methyl orange was used as an indicator in titrating the sodium. The argon was furnished by the Cleveland Wire Works, Cleveland, Ohio, and from their analysis was 99.7% pure, the remaining **0.3%** being chiefly nitrogen. No oxygen and only traces of carbon dioxide were present in the argon.

The platinum–platinum-rhodium thermocouple was calibrated frequently against fixed thermometry points. The latest directions of the Bureau of Standards were very closely followed in the calibration.[13] The freezing points of silver, copper–silver eutectic, and aluminum, and the boiling point of sulfur were taken as the fixed standard points. The silver was of very high purity (99.99%), while the copper and aluminum were Bureau of Standards samples. All of the freezing points were sharp and well defined.

Results

Vapor Pressure.—The vapor pressure data are given in Table **I.** **A** preliminary plot on a log $-1/T$ diagram of these results together with the results of Rodebush and DeVries and Edmondson and Egerton at low pressures indicated that the data over the whole range of pressures could

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[13] *Roeser, Bur. Standards Jour. of Research,* **3, 343** *(1929).*

TABLE I

VAPOR PRESSURES

Run 1

Temp. of sodium, °K.	Argon			Total pressure	Vapor pressure of sodium
	Vol, cc.	Temp., °K.	Pressure, mm.		
924.1	9.58	300.4	743.9	97.2	48.82
939.8				105.6	58.40
950.5				109.9	63.19
973.7	7.73	301.1	744.2	185.6	96.12
989.4				202.5	115.9
999.3				214.2	129.7
1020.1	12.22	300.8	744.1	318.6	158.9
1044.5				365.1	214.2
1063.3				412.8	272.0
1082.9				476.4	350.8
1117.9				581.2	481.5

V_1 = 306.8 cc.; V_2 = 3.32 cc.; T_2 = 373°K.; V_3 = 5.34 cc.; T_3 = 294.2°K.; V_4 = 15.50 cc.; T_4 = 300.0.

Run 2

938.8	11.35	298	746	123.1	65.88
946.9				125.6	68.58
969.5				146.5	93.70
999.5	9.50	298.1	746.4	245.7	139.1
1033				305.5	211.2
1049.9	8.18	298	746.2	395.5	254.0
1070.4				448.5	312.4
1089.3				496.7	378.4
1113.1				479.5	482.5

V_1, V_2, V_3 and V_4 same as in Run 1; T_2 = 373°, T_3 = 293.7°, T_4 = 296.2°.

Run 3

936.7	10.02	297.6	747.8	116.0	67.37
953.2				121.6	73.55
978.7	10.1	297	749.1	216.5	110.1
1011.9				263.3	165.5
1040.7				314.7	228.1

Volumes same as above; T_2 = 373°; T_3 = 292.4°; T_4 = 294.7°.

be satisfactorily represented by a straight line. By the method of least squares a simple equation

$$\log p_{\text{mm}} = A - \frac{B}{T} \qquad (8)$$

was obtained with values for the constants

$A = 7.5165 \pm 0.0075$. $B = 5383.0 \pm 5.7$

This gives a satisfactory value for the probable error (2–3%) but the deviations of individual measurements are large. It is difficult to see how high results would be given by the experimental method, while low results might be explained by failure to obtain saturation with sodium vapor in the vapor space within the bomb although ample time for equilibrium to be established was always allowed. Furthermore, the results of the first run are all below the values given by Equation 8. If we reject the first run as being for some unknown reason unsatisfactory, and consider only the last two runs, we obtain a set of readings which are on the average several per cent. higher and much more consistent. The equation

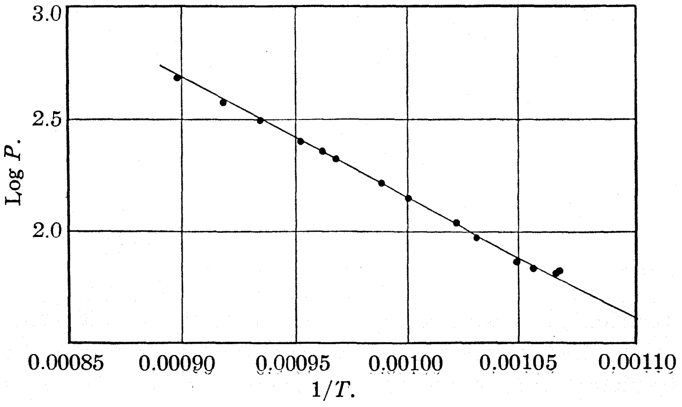
$$\log p_{\text{mm}} = 7.5510 - \frac{5400.0}{T} \qquad (9)$$

fits the low pressure data almost as well as Equation 8 and with the exception of one or two points at intermediate pressures, where larger errors are to be expected, fits the high pressure data very well, as is shown in Table II and Fig. **3.** The two equations are essentially coincident at low

TABLE II

DATA

Data of Rodebush and DeVries and of Edmondson and Egerton			Data of Rodebush and Walters		
	Pressure, mm.				
Temp., °K.	**Calcd. × 10³**	**Obs. × 10³**		**Calcd. × 1**	**Obs. × 1**
454.9	0.0480	0.04929	938	63.3	65.88
473.4	.138	.1412	946.9	70.1	68.58
492.9	.390	.3880	969.5	96.8	93.70
495.9	.469	.4575	999.5	141.6	139.1
513.0	1.07	1.030	1033	210	211.2
514.3	1.42	1.140	1049.9	267	254.0
534.3	2.89	2.852	1070.4	319	312.0
544.4	4.28	4.163	1113.1	392	378.4
570.7	12.50	12.31	1089.3	500	482.5
			936.7	61.1	67.37
			953.2	76.9	73.55
			978.7	107.4	110.1
			1011.9	166.4	165.5
			1040.7	229	228.1



pressures but give values for the boiling point of sodium which differ by 6°. Equation 8 gives a value for the boiling point that is in agreement with the figures given in the literature but these figures might easily be in error by 5–10'.

Vapor Density.—Vapor density results are given in Table III. Measurements were made at two different temperatures, 705.8 and 570.5." The effect of rate of flow on the amount of sodium deposited was studied and it was found that fairly consistent results could be obtained when the rate was between 10 and 25 cc. per minute. A blank run with no gas flowing at 705.8' showed that 0.04–0.05 g. of sodium would diffuse into the outer tube in three hours. The apparent molecular weights in Table III have been calculated using Equation 8. A markedly different result is obtained using Equation 9 and the average values for apparent molecular weights (omitting runs where the rate of flow was too fast) are tabulated below.

TABLE III

VAPOR DENSITY DATA

No.	Rate of flow, cc. per min.	Vol. argon, liters	Temp. of argon, °C.	Barometer, mm.	Sodium, g.	Mol. wt.
			Temperature of sodium, 705.8°			
31	22.2	2.0	24.2	739.1	0.3055	24.2
32	25.6	2.0	23.5	745.5	.3077	24.3
33	25.0	2.0	24.3	745.9	.3208	25.4
34	22.4	2.0	24.0	753.0	.3089	24.5
35	16.1	2.5	'22.9	740.9	.4078	25.7
36	15.3	2.5	21.3	740.9	.3920	24.5
37	10.5	2.0	23.3	740.6	.3190	25.2
38	25.9	2.0	20.0	746.8	.3156	24.6
39	15.6	2.0	23.6	746.5	.3202	25.2
40	27.4	2.0	20.3	749.8	.3064	23.8
41	23.3	2.0	23.3	741.6	.3144	24.7
42	20.0	2.0	22.0	742.3	.3128	24.5
43	29.9	2.0	25.0	746.5	.3001	23.9
44	15.7	2.0	25.2	746.4	.3089	24.7
45	35.1	2.0	27.4	745.0	.2696	23.3
46	9.2	2.0	26.8	744.5	.3199	25.7
			Temperature of sodium, 570.5°			
47	18.4	2.5	22.8	746.5	0.0472	26.1
48	16.4	2.5	22.1	743.7	.0458	25.3
49	17.4	2.5	23.2	741.0	.0435	24.0
50	18.1	2.5	22.0	745.7	.0449	24.7
51	19.2	2.5	22.0	744.9	.0490	26.9
52	19.1	2.5	23.6	739.2	.0485	26.9
53	19.7	2.5	25.7	734.9	.0474	26.6
54	11.6	2.5	21.4	735.6	.0508	27.9

Argon collected over water at same temperature as the gas.

TABLE IV

Temp., °C.	Equation 8 Pressure, mm.	Equation 8 Mol. wt.	Equation 9 Pressure, mm.	Equation 9 Mol. wt.
705.8	104.2	25.0	108 2	24.1
570.5	13.5	26.0	14.0	25.1

These results on vapor density will be discussed in a later paragraph.

Errors.—The constant errors in the vapor pressure measurements should not be greater than the calculated probable error. The uncertainty in the temperature measurements is very small since the fused salt bath was very easily controlled and the thermocouple was carefully calibrated. The pressures given are in mm. of mercury at room temperature since the accuracy does not justify calculation to 0°. The estimation of the external volumes of the apparatus corresponding to different zones of temperature involves an uncertainty which has been estimated to give a probable error of 0.5%. In the vapor density determinations the probable errors in the determination of gas volumes and amounts of sodium vaporized were certainly less than 1%. The temperature control was more uncertain in the furnace than in a fused bath but the temperature was held constant to 0.5° and explorations with the thermocouple indicated that a zone of nearly constant temperature extended for a considerable distance in either direction from the point where the sodium was vaporized.

The Dissociation Equilibrium in Sodium Vapor.—There appears to the authors to be no question of the existence of an appreciable amount of Na_2 molecules in sodium vapor. Postponing for the moment the incontrovertible evidence of band spectra, we believe the vapor pressure curve by itself is evidence for the existence of molecules. The vapor pressure data are of sufficient accuracy to show that a straight line is obtainable on the log p–$1/T$ plot and this straight line indicates some abnormality of vapor density, as has been stated before. At the low pressures involved, the natural assumption to make is that the abnormal vapor density is due to the presence of molecules.

The results of Table IV, no matter which equation is preferred, are impossible to explain, however, because they indicate that the apparent molecular weight of the saturated vapor decreases with increasing temperature. This could only be true if the heat of dissociation were greater than the apparent molal heat of vaporization, but if that were true it can readily be calculated that'the apparent molecular weight of sodium would be far greater than the observed values in Table IV. The authors are, therefore, inclined to reject the results for vapor density at the higher pressure and temperature for the same reason that they are inclined to reject low values for vapor pressure. It seems probable that saturation could not be obtained, perhaps because of rapid diffusion of the vapor to the cooler portion of the tube. This difficulty would not be remedied by reducing the rate of flow of the inert gas. On the other hand, the authors now believe the results obtained at 570.5' to be reliable, although the results are higher than those obtained by Haber and Zisch with the same method in the same temperature range. We have supposed the experimental errors to be greater because of the smaller amounts of sodium transferred but these difficulties are trivial compared to the difficulty of saturating the inert gas. The results at the lower temperature appear on the whole the more consistent. Accordingly we believe Equation 9 to represent the vapor pressure of sodium with satisfactory accuracy and the vapor density as obtained with this equation at 570.5' to be substantially correct.[14] Gibson and Heitler[15] have derived an equation relating the dissociation constant of a diatomic gas to the heat of dissociation, and certain constants calculated from spectroscopic data. Their equation may be written

$$\log K = -\frac{\Delta H_o}{4.575T} + \frac{3}{2}\log\left(\frac{\pi mkT}{h^2}\right) - \log\frac{8\pi^2 I}{h_2} + \log\left(1 - e^{-h\nu/kT}\right) + \log 2 + \log(2j + 1) \qquad (10)$$

Here K is the constant of Equation 10 above expressed in c. g. s. units, ΔH_o is the heat of dissociation at absolute zero, h is Plancks' constant, I is the moment of inertia of the Na_2 molecule or 179.5 X 10^{-40} g. cm.^{2}, v is the vibrational frequency of the Na_2 molecule or 158.5 cm.$^{-1}$ and j is the angular momentum of the sodium atom, which is $^1/_2$, since its ground state is ^2S. The sodium atom has a nuclear spin of several half units, and a term $2 \log (2s + 1)$ should be introduced into the equation were it not for the fact that there are two kinds of sodium molecules similar to ortho and para hydrogen. There are $(s + 1)(2s + 1)$ possible spin eigen-functions that are symmetric in the nuclei and $s(2s + 1)$ that are antisymmetric in the nuclei. This gives a total multiplicity of $(2s + 1)^2$ for the rotational levels, which just cancels the term $2 \log (2s + 1)$ for the atoms.

The only uncertainty involved in the calculation of the constant for the dissociation equilibrium by Equation 11 is the value to be used for the heat of dissociation of the Na_2 molecule. The value calculated by Loomis is 1.0 ± 0.1 volt and Kinsey[16] has estimated that it may be as low as 0.84 volt = 19,360 cal. It does not seem probable that it can be much less than this. Using this figure we calculate K for the equilibrium $Na_2 \rightleftharpoons 2Na$ to be 10^5 (pressure in c. g. s. units) at 570.5' and the ap-

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[14] Our confidence in these results is greatly strengthened by the receipt of a private communication from R. Ladenburg in which he informs us that he has repeated the work of Haber and Zisch at the Kaiser Wilhelm Institute with great care and has obtained results that are in substantial agreement with ours.

[15] Gibson and Heitler, *Z. Physik,* 49, 465 (1928).

[16] Kinsey, *Proc. Nat. Acad. Sci.,* 15, 37 (1929).

parent molecular weight to be 26.0. This is perhaps as good agreement as one can hope for. An apparent molecular weight of 27 is predicted for sodium vapor at 705.8° and this value cannot be reconciled with the values given in Table IV.

The Entropy of Sodium Vapor.—Rodebush[17] calculated the entropy of sodium vapor and showed it to be in close agreement with the theoretical value predicted for an atom in ^2S state. This calculation is confirmed by our new measurements since the saturated vapor is shown to be largely monatomic at lower temperatures and the vapor pressure measurements of Rodebush and DeVries are confirmed. Theoretically the entropy should be greater than that calculated by an amount $R \ln (2s + 1)$, and if the heat capacity of metallic sodium were measured to a sufficiently low temperature, a heat effect would doubtless be found corresponding to the change in orientation of the nuclear spin.[17,18] This heat effect is so small and at so low a temperature that it is not likely to be observed, although the corresponding entropy change is not negligible.

Summary

The vapor pressure of sodium has been measured over the temperature range from 650–850°.

The preferred vapor pressure equation is

$$\log p_{\text{mm.}} = 7.5510 - \frac{5400.0}{T}$$

The equation gives good agreement with previous data down to pressures of 10^{-4} mm.

The apparent molecular weight of saturated sodium vapor has been determined at 570.5 and 705.8°. The values at the lower temperature are believed to be more nearly accurate and are in fair agreement with the value calculated from spectroscopic data.

URBANA, ILLINOIS

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[17] Rodebush, *ibid.*, **13**, 185 (1927).

[18] *Phys. Rev.*, 35, 210 (1930).

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

ZIRCONIUM. VI. USE OF DISPERSOIDS IN THE DETECTION OF TRACES OF POTASSIUM BY ZIRCONIUM SULFATE

BY RUFUS D. REED AND JAMES R. WITHROW

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The results of an investigation of the effect of the addition of a dispersoid of potassium zirconium sulfate in shortening the time required for a test for potassium by zirconium sulfate indicated that the time factor is materially reduced by adding the dispersoid. The sensitivity of zirconium sulfate for potassium is slightly greater in the presence of a dispersoid than in its absence.

The tardy formation of crystals in supersaturated solutions is commonly ascribed to lack of suitable nuclei. A frequently used method of overcoming such supersaturation has been to add a crystal of the desired substance. Where traces of constituents are sought, however, the addition of such a crystal would introduce a comparatively large amount of the product, hindering the detection of any minute quantities; hence the method is of little value in analytical chemistry. It would appear feasible that any supersaturation tendency in testing for traces of substances could be eradicated by introducing into the solution tested a drop of a liquid containing a very minute amount of the precipitate expected, in dispersoid state. If the solution tested contained no appreciable amounts of the substance to form that added in dispersoid form, then the dispersoid should not cause an increasing turbidity in the solution; but if there is any of the substance present, the turbidity should increase due to the nuclei growing and multiplying in number or size. To avoid adding appreciable quantities of solute, we have for some time in this Laboratory, added a controlled trace of the precipitate with the reagent, as has doubtless been done by others. We now find as far as information is available that Forbes[1] as early as 1911 in determining the solubility of silver chloride in chloride solutions overcame the supersaturation tendency "by adding, on the end of a stirring rod, quantities of precipitated silver chloride so minute as to produce no visible turbidity in 50 cc. of pure water." The method does not seem to have come into general use. This paper reports the application of the procedure or principle to the simple case of the detection of potassium by zirconium sulfate.

Experimental

Materials.—The zirconium sulfate solution (containing 11.31% of zirconium sulfate) and the potassium sulfate solutions used were those described in our previous work.[2]

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[1] Forbes, THIS JOURNAL, 33, 1938 (1911).

[2] Reed and Withrow, *ibid.*, 50, 2986 (1928).

Dispersoid.—The dispersoid of potassium zirconium sulfate was obtained from a mixture of dilute potassium sulfate solution and the zirconium sulfate reagent which had reacted to form a precipitate. Knowing the concentration of potassium in the original mixture of 2 cc. to be 2.4 mg. of potassium and assuming 30 drops to *a* cubic centimeter of solution, one drop of this mixture would add not over 0.04 mg. of potassium to the solutions tested.

Procedure.—The procedure was the same as that given under the general procedure in the previous work,[3] except that after the reaction mixture had stood for an hour at room temperature, *a* drop of *a* solution containing a suspension of potassium zirconium sulfate was added. After the completion of the test for potassium by zirconium sulfate and the dispersoid mixture, the solutions were filtered and the filtrates showed the presence of potassium when tested by sodium cobaltic nitrite after first throwing the zirconium into a complex ion with tartaric acid and sodium hydroxide according to the method previously reported.[4] The results appear in the table.

TABLE I

SUMMARY OF EFFECT OF DISPERSOID ON DETECTION OF POTASSIUM WITH ZIRCONIUM SULFATE

Expt.	K per sample, g.	Results with dispersoid added	Results with no dispersoid added
1	0.00119	Opal. 1 hr. r. temp.; small ppt. 0.5 hr. 0°	Opal. 1 hr. r. temp.; cloudy 0.5 hr. 0°
2	.00095	Opal. 1 hr. r. temp.; cloudy 0.5 hr. 0°; ppt. 1 hr. 0°	Opal. 1 hr. r. temp.; cloudy 0.5 hr. 0°; ppt. 1.25 hr. 0°
3	.00078	Cloudy 0.5 hr. 0°; small ppt. 2 hr. 0°	Opal. 0.5 hr. 0°; ppt. 3 hr. 0°
4	.00048	Opal. 0.5 hr. 0°; ppt. 3 hr. 0°	Very sl. cloudy 1.5 hr. 0° cloudy 5 hr. 0°
5	.00032	Slightly opal. 0.5 hr. 0°; ppt. 3 hr. 0°	Clear 5 hr. 0°
6	.00000	Slightly opal. 0.5 hr. 0°; unchanged 5 hr. 0°	Clear 5 hr. 0°

Total volume, 2 cc.; zirconium sulfate present, 0.1131 g.

Discussion.—These results were typical of about 80 experiments. Comparing the sensitivity with and without the dispersoid indicated that the addition of the dispersoid increased the sensitivity of zirconium sulfate for potassium from 0.48 mg. of potassium (0.05% elemental potassium or 0.006 molal potassium sulfate) to 0.32 mg. (0.03% elemental potassium or 0.004 molal potassium sulfate), Expts. 4 and 5.

Comparing the time needed for securing the test with a dispersoid present and without a dispersoid showed that the presence of the dispersoid

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[3] Reed and Withrow, THIS JOURNAL, 50, 1515 (1928).

[4] Reed and Withrow, *ibid.*, 51, 3238 (1929).

shortened the time in Expt. 2 with 0.95 mg. of potassium by 15 minutes, and in Expt. 4 with 0.48 mg. of potassium, two hours were saved.

In Expts. 4 and 5 containing 0.48 mg. and 0.3 mg. of potassium, respectively, the test for potassium in the filtrate (not removed by zirconium sulfate) was very faint and appeared only after allowing the test to stand for forty minutes.

Summary and Conclusions

1. "Seeding" by adding a solute dispersoid furnishes suitable nuclei for initiation of visible precipitation without introducing appreciable quantities of the material to be detected.
2. The addition of a drop of a dispersoid of the desired product hastens the detection of potassium by zirconium sulfate.
3. The sensitivity of zirconium sulfate reagent for potassium was increased through the presence of the dispersoid from 0.48 mg. of potassium to 0.32 mg. per 2 cc. of reaction mixture.
4. The zirconium sulfate reagent did not completely remove potassium from solution.

COLUMBUS, OHIO

THE SORPTION OF ORGANIC VAPORS BY HIGHLY EVACUATED, ACTIVATED SUGAR CHARCOAL[1]

BY JAMES W. McBAIN, H. P. LUCAS AND P. F. CHAPMAN

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It is of the greatest interest to determine in how far sorption data for a given specimen of charcoal may be made reproducible through improvements in the preliminary treatment, and then to ascertain in how far differently activated specimens of the same charcoal yield sorption data conforming to a definite type. In previous communications,[2] it has been increasingly shown that improvements in the preliminary evacuation of a given specimen of charcoal greatly affect not merely the position, but also the form of the sorption curve. This becomes especially noticeable as the cleansing of the charcoal through evacuation is made very thorough. It is found advisable to evacuate for a long period at as high a temperature as possible in a high vacuum, then to displace some of the impurities still sorbed on the charcoal by admitting to the charcoal some of the liquid to be investigated and repeating the thorough evacuation before commencing the experiment.

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[1] These experiments were carried out at the University of Bristol, England, in 1925–1927 inclusive.

[2] A. M. Bakr and J. E. King, J. *Chem. Soc.*, 119, 454 (1921); A. M. Bakr and J. W. McBain, THIS JOURNAL, 46, 2718 (1924); J. W. McBain, *Nature*, 117, 550 (1926); J. W. McBain and G. T. Britton, THIS JOURNAL, 52, 2198 (1930); J. W. McBain, D. N. Jackman, A. M. Bakr and H. G. Smith, *J. Phys. Chem.*, 34 (1930).

This communication describes experiments with seven organic chemicals, using four air and steam activated charcoals made from the same pure sugar charcoal.[3] Definite regularities have been found, and it is shown that some specimens of charcoal possess a saturation value in that they sorb as much vapor at low as at high pressures, whereas other specimens exhibit sorption which definitely rises even in the higher ranges of pressure.

A sorption balance, such as that of McBain and Bakr,[4] used in a tube which remains sealed throughout the course of the experiments, proved highly advantageous for the study of these differential effects.

Experimental

The liquids were Kahlbaum's best and were redistilled before use. Four charcoals prepared from the same sugar charcoal were employed and are designated as follows.

"Air and Vacuum B."[5]—Prepared by A. M. Bakr in 1923 by heating in *vacuo* in a silica flask for fifty-six hours in the tip of the blowpipe flame, admitting a very slow current of air during the first six hours.

"Air C."[5]—Prepared by H. G. Smith in 1925 by heating for twelve hours in an unglazed porcelain tube at 1140° (measured), a slow current of air being passed throughout and burning away 20% of the charcoal.

"Steam D."[5]—Activated in 1925 by H. H. M. Wright by heating in a silica flask at 700° for forty-five minutes in a current of steam and continued heating for ten minutes.

"Steam E."—Activated by Chapman in 1927 by heating in a silica flask at 650° (measured) for thirty minutes and then blowing a current of steam directly on the charcoal for forty-five minutes during which the flask was shaken, the temperature falling to 600°; the charcoal was heated for ten minutes further and on cooling resembled a fluid.

It was found that springs of fused silica increase in length when heated under load, although the elastic constant is far less affected. No change can be detected during six weeks at 40°, and the change at higher temperatures rapidly diminishes as heating is continued.[6] These effects are readily obviated by heating the spring under load at 300° for two days before calibration. Recalibration at the end of an experiment shows this to be effective. The initial increase of the length of a spring under a load of 0.26 g. is about 0.0028 cm. per hour at 440°.

About 0.1 g. of charcoal was used in a bucket of gold foil weighing less than 0.1 g. It was found by blank experiments that the weight of vapor sorbed by the gold bucket was far less than the number of figures to which the weight of vapor sorbed by charcoal was read.[7]

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[3] For analyses and tests see previous communications.

[4] J. W. McBain and A. M. Bakr, THIS JOURNAL, 48, 690 (1926).

[5] See previous communications for other measurements with this charcoal. The conditions of activation were not ideal and do not afford a legitimate comparison between the possibilities of air and steam activation; for example, in the latter case the temperature was too low.

[6] The physical properties of fused silica are well known to be undefined (Footnote 7 of Ref. 2). We have on several occasions had a spring break when carrying less than a previous load, and, on one occasion, we have seen a spring rather suddenly change its length and sensitivity.

[7] Using a gold bucket of 22.6 sq. cm. area and a spring extending 0.694 mm. per milligram at 120°, extension was not definitely noticeable until the vapor pressure of toluene was 250 mm., and it was 0.008 cm. when the pressure of the toluene was be-

Procedure

The experimental method required the constant presence of a body of pure liquid whose temperature may be arbitrarily adjusted so that the charcoal within the same sealed tube, but at higher temperature, may be exposed to any desired pressure of the vapor. It is vital that the charcoal should be drastically cleansed by heat and evacuation, and during this process the liquid to be used must remain within a sealed bulb (A in Fig. 1). Only after the final evacuation, when the main tube has been sealed, is this bulb A broken.

Preliminary Evacuation.—The charcoal and most of the sorption tube (see Fig. 1) were heated to 440° for seventy-five minutes during which a vacuum was very slowly applied. Evacuation was continued for three hours after the pressure had fallen below 10^{-4} mm. at 440°. (The bulb X with supporting hook rests on four projections in the glass to allow free passage.) Thereupon, after taking a zero reading of the length of the spring, the bottom of the tube containing the sealed bulb of liquid B, to which is attached by a solid stem a sealed bulb containing iron filings, is cooled with solid carbon dioxide or liquid air. The bulb is then raised by an electromagnet and broken. The whole is left at room temperature for some time to allow the vapor to displace foreign gases on the charcoal.

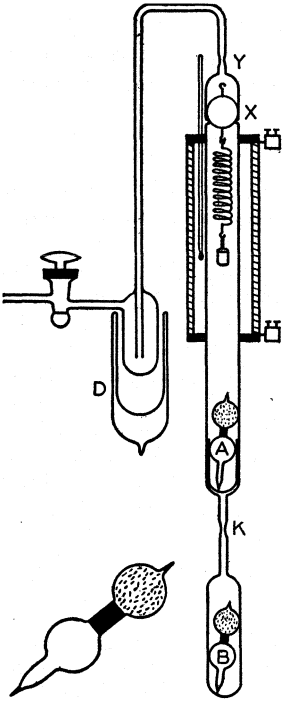

Fig. 1.—The sorption apparatus during evacuation, showing **enlarged detail of** the sealed bulb **of liquid**, B.

Final Evacuation.—The Dewar vessel D, filled with liquid air, is placed in position very gradually in order to avoid blowing charcoal out of the bucket. The tube is sealed off at K. The whole is then evacuated with the same care as before, but it takes several hours to bring the charcoal to 440° without blowing it out of the bucket. The time taken to attain a high vacuum is now much greater. While the vacuum pump is still working, the tube is finally sealed off at Y and is not reopened until the investigation is complete. The sealed bulb of liquid, A, is then cooled and broken as previously described.

Thermostats.—During an experiment the bottom of the sorption tube is immersed in mercury containing a thermometer. The whole sorption tube is placed within a wider glass tube which is heavily covered with asbestos on the outside and has a narrow slit in front and back running the length of the tube for purposes of observation. Outside this is wound heavy nichrome wire covered over again with asbestos. Current is led through the nichrome wire, using three terminals, a common one in the middle, and one at each end. Asbestos packing is placed outside the sorption tube at the middle terminal and at the top of the sorption tube, the furnace being closed above. A thermometer is placed between the sorption tube and the outside furnace beside the bucket of charcoal. In a blank experiment it was found that the thermometer placed within the vapor at 120° read 1.3° higher than that outside the tube. The whole is enclosed in a case with glass windows.

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tween 300 and 600 mm. This corresponds to 5×10^{-6} g. of toluene per sq. cm. of gold foil or a film approximately 5×10^{-6} cm. deep.

Commercial air ovens were found unsatisfactory, even although heating coils were inserted around the tubes where they passed through apertures. For low temperatures the apparatus was modified to admit of surrounding the bottom of the sorption tube with a Dewar flask containing a freezing mixture whose temperature was read by a pentane thermometer, a thermocouple being used to cheek constancy. All thermometers were calibrated against standards supplied by the National Physical Laboratory.

The charcoal was kept in contact with vapor for several days at 120° (or 205°) before any readings were taken, and not less than two hours was allowed between duplicate readings. Under these conditions Chapman observed but little effect of time. He avoided any condensation of liquid upon the charcoal.

TABLE I

ACETIC ACID.[a] "AIR C" CHARCOAL. 120° ISOTHERM BY P. F. C.

Experiment 5[b]

p	x/m	p	x/m	p	x/m[c]
23.1	0.204	88.9	0.334	169.8	0.383
27.3	.224	128.6	.359	142.6	.374
36.9	.255	132.0	.365	67.8	.321
37.9	.264	163.8	.379	39.5	.264
48.1	.280	175.3	.389	23.8	.221
58.6	.304	266.8	.414	16.4	.185
91.6	.329	483.4	.440	13.5	.162

[a] p_s = 794 mm. at 120°, 6500 mm. at 205°. [b] Final vacuum 10^{-5} mm. [c] Desorption.

TABLE II

ACETIC ACID. "AIR C" CHARCOAL. 120° ISOTHERMS BY H. P. L.

Experiment 1

p	x/m	p	x/m
14.5	0.178	330	0.424
77	.326	535	.435
125	.357	245	.414
127.5	.361	695	.450
204	.406	26.5	.24

Experiment 18

p	x/m	p	x/m
15	0.183	390	0.415
32	.258	193	.397
97.5	.361		

Experiment 19

p	x/m	p	x/m
14	0.198	660	0.461
30	.265	590	.457
58	.318	545	.453
505	.446	123	.381
276	.421	3.3	.082
725	.463		

TABLE III

ACETIC ACID. "STEAM D" CHARCOAL. ISOTHERMS BY H. P. L.

Experiment 2

At 120°

p	x/m
13.5	0.111
27.5	.112
116	.141
202.3	.148
153	.146
675	.156
330	.150
56	.133

At 205°

p	x/m	p	x/m
17.5	0.0269	1070	0.129
41.5	.0435	202.3	.091
125	.0770	2900	.140
730	.122	4630	.141
2195	.137	5450	.141

TABLE IV

TOLUENE.[a] "AIR C" CHARCOAL. 120° ISOTHERMS BY P. F. C.

Experiment 2[c]

p	x/m	p	x/m	p	x/m[b]
81.6	0.267	264.6	0.294	535 8	0.311
34 5	.238	383.4	.304	416.8	.304
51.1	.252	567.0	.310	225 2	.293
105.8	.276	613.2	.314	95 3	.270
131.9	.280	746 5	.318	26 3	.228
183.4	.290	869	.325	7.6	.199

Experiment 3[d]

p	x/m	p	x/m	p	x/m
68.3	0 296	641	0.354	68.3	0.300[b]
130.0	.321	752	.359	52.4	.290[b]
207.7	.332	325	.341[b]	28.4	.272[b]
355	.338	279.5	.340[b]	25.4	.263[b]
399 5	.342	144	.325[b]	7.8	.252[b]
528	.349	93.5	.311[b]	0.006[e]	.180[b]

[a] p_s = 988 mm. at 120°, 6451 mm. at 205°. [b] Desorption. [c] Preliminary evacuation five hours at 10^{-5} mm.; final evacuation six and one-half hours at 2 × 10–4 mm. Forty-five readings were taken, all of which fell on a smooth curve. The results are omitted from the graph because two turns of the spiral spring were caught in each other. [d] Preliminary evacuation seven hours at 10^{-5} mm.; final evacuation sixteen hours at 10^{-5} mm. [e] Liquid surrounded by solid carbon dioxide and ether.

TABLE V

TOLUENE. "AIR C" CHARCOAL. ISOTHERMS BY H. P. L.

Experiment 7		Experiment 10			
At 120°		At 120°		At 205°	
p	x/m	p	x/m	p	x/m
25	0.238	27	0.244	32	0.140
100	.289	62	.272	99	.190
178	.302	92	.283	2234	.291
223	.316	155	.298	263	.233
259	.323	230	.309	2583	.296
778	.332	460	.326	2965	.296
93 5	.293	790	.331	690	.272
74	.291	1020	.335	820	.276
67	.285	360	.321	850	.285
47.7	.281				

TABLE VI

TOLUENE. "AIR AND VACUUM B" CHARCOAL. 120° ISOTHERM BY H. P. L.

Experiment 9

p	x/m	p	x/m
845	0.140	820	0.142
27	.111	970	.141
107	.133	990	.144
200	.137	970	.141
250	.139	980	.141
720	.141	560	.141

TABLE VII

TOLUENE. "STEAM D" CHARCOAL. 120° ISOTHERM BY H. P. L.

Experiment 8

p	x/m	p	x/m
88	0.132	115	0.138
460	.139	92	.133
610	.139	80	.132
910	.142	25	.121

The data are given in Tables I–XIV where p is the vapor pressure in millimeters, and x/m is the sorption in grams per gram of charcoal. The vapor pressures were calculated using Dühring's rule with data obtained from Landolt–Börnstein "Tabellen," 1923.[8] p_s, the saturation pressure, is the vapor pressure of the liquid at the temperature of the isotherm.

TABLE VIII

TOLUENE. "STEAM E" CHARCOAL. 120° ISOTHERM BY P. F. C.

Experiment 4[a]

p	x/m	p	x/m	p	x/m
32 0	0.180	493	0 212	223	0 204[b]
22 4	.174	571 3	.214	98 2	.196[b]
92 8	.195	658	214	74.9	.193[b]
173 7	.202	854	.215	52 2	.188[b]
334.1	208	474	.213[b]	7.8	.152[b]

[a] Preliminary evacuation eleven hours at 10^{-5} mm.; final evacuation sixteen and one-half hours at 10^{-4} to 10^{-5} mm. [b] Desorption.

TABLE IX

HEXANE.[a] "AIR C" CHARCOAL. 120° ISOTHERM BY H. P. L.

Experiment 23

p	x/m	P	x/m	P	x/m
179	0.219	588	0.249	2100	0.268
279	.229	1050	.255	2800	.273
410	.239	1600	.263	1520	.263

[a] p_s = 2982 mm. at 120°.

TABLE X

HEPTANE.[a] "AIR C" CHARCOAL. ISOTHERMS BY H. P. L.

Experiment 17

At 120"		At 120"	
p	x/m	p	x/m
42	0 226	490	0.269
285	.259	735	.274
618	,272	153	.251
848	,276	1260	.282
1080	.280		

Experiment 22

At 120"		At 120"	
51	0.219	270	0.262
108	.236	370	.264
119	,239	614	.266

Experiment 24

At 120"		At 205°	
P	x/m	p	x/m
46	0.219	59	0.150
90	.234	125	.166
138	.244	225	.185
452	.259	300	.194
578	.263	1530	.226
1047	.272	990	.219
1230	.284	1230	.228
1100	.279	1930	.231
660	.265	1700	.233
264	.252	690	.215

[a] p_s = 1367 mm. at 120°, 8000 mm. at 205°.

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[8] Data for toluene were obtained from N. W. Krase and J. B. Goodman, *Ind. Eng. Chem.*, 22, 13 (1930).

TABLE XI

OCTANE.[a] "AIR C" CHARCOAL. ISOTHERMS BY H. P. L.

Experiment 12

At 120°		**At** 120°		**At** 205°		**At** 205°	
p	x/m	p	x/m	p	x/m	p	x/m
20	0.249	515	0.289	340	0.235	1300	0.251
52	.263	550	.289	1540	.250	2075	.253
150	.280	630	.289	1650	.252	590	.238
380	.287	615	.289	1720	.252	44	.187

Experiment 13

At 120°		**At** 120°		**At** 205°	
p	x/m	p	x/m	p	x/m
37	0.259	320	0.286	38	0.185
47	.264	118	.281	115	.217
105	.279	87	.276	188	.227
180	.284	18	.243	650	.242
460	.288	60	.265	1290	.250
400	.288	200	.283	2150	.258

[a] p_s = 645 mm. **at** 120°, 4500 mm. **at** 205°.

TABLE XII

DECANE.[a] "AIR C" CHARCOAL. ISOTHERMS BY H. P. L.

Experiment 16

At 120°		**At** 120°		**At** 205°	
p	x/m	p	x/m	p	x/m
2.9	0.226	4	0.233	6	0.166
71	.273	59	.270	11	.184
14	.250	92	.274	165	.230
22	.263	158	.282	560	.247
115	.276	215	.291	1310	.256

Experiment 20

At 120°				**At** 205°			
p	x/m	p	x/m	p	x/m	p	x/m
26	0.267	44	0.281	265	0.246	314	0.254
42	.271	140	.295	2087	.264	110	.234
120	.292	177	.301	530	.256	15	.195
225	.303	215	.305	750	.261	10	.182
167	.306			875	.262		

[a] p_s = 245 mm. **at** 120°, 2314 mm. at 205°.

TABLE XIII

ACETONE.[a] "AIR C" CHARCOAL. 120° ISOTHERM BY F. P. C.

Experiment 6

p	x/m	p	x/m	p	x/m
201.4	0.282	383	0.322	1353	0.373
209.5	.286	487	.335	1741	.388
253.5	.297	660	.349	1646	.391
307.7	.300	915	.389	2690	.404
437	.325	938	.366	3420	.411

[a] p_s = 5000 mm. **at** 120°.

TABLE XIV

METHYL ALCOHOL.[a] "AIR C" CHARCOAL. ISOTHERMS BY H. P. L.

At 40°		Experiment 25 At 40°		At 120"	
p	*x/m*	*p*	*x/m*	*p*	*x/m*
110	0.325	181	0.350	230	0.0459
31	.206	170[b]	.342	1200	.206
11	.082	165	.346	900	.174
90	.307	105	.326	2900	.289
31	.205	101	.324	3800	.309
46	.247	96	.320	2000	.257
113	.331	255	.355	1780	.249
200	.351	217	.350	720	.143

[a] p_s = 260.5 mm. at 40°, 4751 mm. at 120°. [b] The experiment was then left for one and one-half months before the further readings were taken.

Discussion

The most striking result of our experiments in this and the previous communications is that most of the sorption of vapors occurs at pressures amounting to only a few hundredths of the saturated vapor pressure at that temperature. Indeed, in several cases the sorption is only halved when the pressure is but one ten-thousandth of saturation. It needs no emphasis that this excludes the hypothesis of capillary condensation of liquid as a significant factor in the sorption of vapors by activated charcoal.

Differently activated samples of the same charcoal exhibit characteristically different behavior. In this as in previous communications, steam activated charcoal was not nearly as active as the best air activated charcoal. Oxidation of an appreciable fraction of the charcoal at 1140° yielded a highly active charcoal, capable

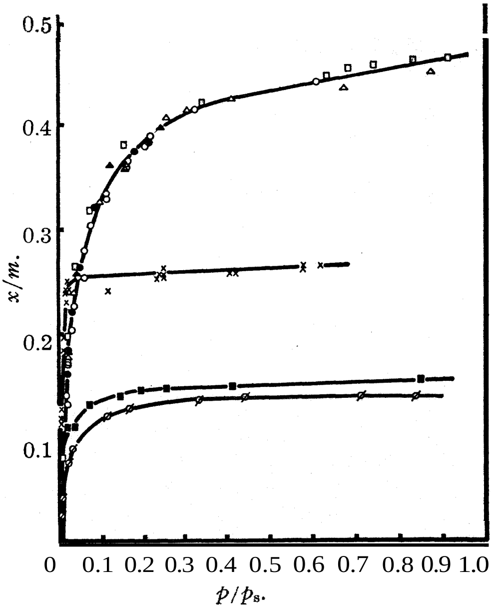

Fig. 2.—Sorption of acetic acid on charcoal. ○, P. F. C., Expt. 5, 120°, "Air C"; ●, P. F. C., Expt. 5, 120°, "Air C", desorption; △, H. P. L., Expt. 1, 120°, "Air C"; A, H. P. L., Expt. 18, 120°, "Air C"; □, H. P. L., Expt. 19, 120°, "Air C"; ■, H. P. L., Expt. 2, 120°, "Steam D"; ø, H. P. L., Expt. 2, 205" "Steam D"; ×, M. C. R.,[a] 120°, "Air and Vacuum B."

[a] Data obtained by Miss M. C. Rattue in 1925, using the method here described, the same conditions of time and temperature of evacuation and the same vacuum.

of sorbing from 30–45% of its own weight of various organic liquids. This charcoal, however, definitely does not show a "saturation value," for, with the possible exception of octane, the sorption continues to rise distinctly in the higher ranges of pressure.

Our results confirm the independent experiments of those who have previously studied the specimen of air activated charcoal that was given the long vacuum treatment at high temperature by Bakr. There is for practical purposes with a number of substances a saturation value. For example, reference to Table VI and Fig. 3 shows that when the pressure of the toluene vapor is only 23% of the vapor pressure of liquid toluene, the amount of sorption x/m is 0.139, while at 96% of the vapor pressure it is increased merely to 0.141. Indeed, the value of the sorption is, within the experimental error, 0.141 g. of toluene to 1 g. of charcoal throughout the upper half of the possible range of pressure. Other substances with the same charcoal may show far less tendency to approach a saturation value. This is notably the case with methyl alcohol and acetone.

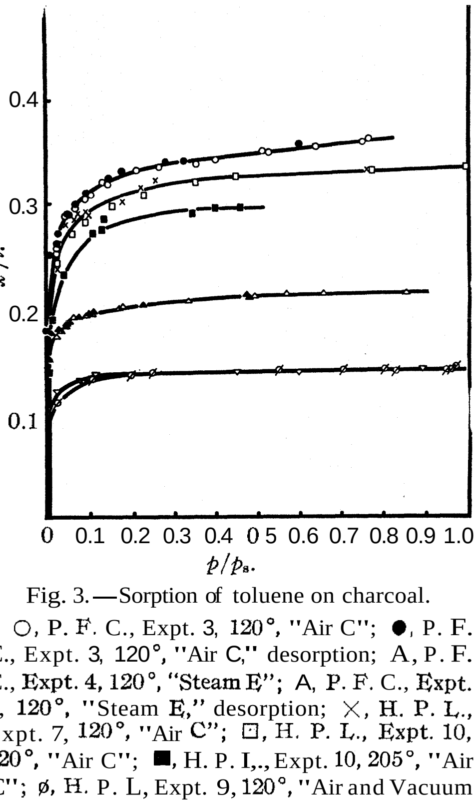

Fig. 3.—Sorption of toluene on charcoal.

O, P. F. C., Expt. 3, 120°, "Air C"; ●, P. F. C., Expt. 3, 120°, "Air C," desorption; A, P. F. C., Expt. 4, 120°, "Steam E"; A, P. F. C., Expt. 4, 120°, "Steam E," desorption; X, H. P. L., Expt. 7, 120°, "Air C"; ☐, H. P. L., Expt. 10, 120°, "Air C"; ■, H. P. I,., Expt. 10, 205°, "Air C"; ø, H. P. L, Expt. 9, 120°, "Air and Vacuum B"; ∇, H. P. L., Expt. 8, 120°, "Steam D."

We incline to regard the form and position of our sorption curves as being more typical of the true behavior of charcoal toward vapors than those obtained in the best studies from other laboratories, such as the results of Coolidge[9] and of Goldmann and Polanyi.[10] We base this, first, upon the consideration that in our experiments the residual impurities still present within the charcoal and the apparatus are constant throughout, and, second, upon our experience that very slight amounts of impurity, such as remain in spite of fairly good evacuation of the charcoal, suffice to lower the values of sorption observed, most notably in the lower range of pressures, so that the graphs assume more

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[9] A. S. Coolidge, THIS JOURNAL, 46, 596 (1924).

[10] F. Goldmann and M. Polanyi, *Z. physik. Chem.*, 132, 321 (1928).

nearly the appearance of those of the authors to whom specific reference has just been made. We have gained the impression that, with still more perfect evacuation, greatly prolonged, at the highest attainable temperatures, the typical sorption curve for charcoal would approach even more closely a form showing first a nearly vertical portion with the whole of sorption occurring at very low relative pressures, followed by an approximately horizontal line corresponding to no further increase of sorption over all the higher range of pressure.

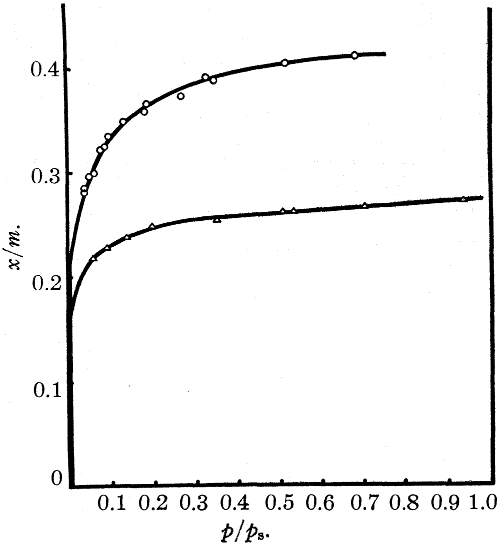

Fig. 4.—Sorption of hexane and of acetone by "Air C" charcoal at 120°. A, H. P. I,., hexane, Expt. 23; O, P. F. *C.*, acetone, Expt. 6.

The form of this curve appears to be fairly independent of temperature. Throughout the higher range of sorption, the graphs for different temperatures run approximately parallel. Rise of temperature, as always, diminishes the weight of sorbed vapor which the charcoal can contain. The

TABLE XV

MEASUREMENTS BY **H. P. I,.** WITH "AIR C" CHARCOAL FOR p/p_s = **0.5**

Vapor	120°	205°	Ratio
Hexane	0.262	..	..
Heptane	.270	(0.24)	1.125
Octane	.287	.254	1.130
Decane	.293	.262	1.118
Toluene	.327	.296	1.105
Acetic acid	.428	..	...
Acetone	.403	..	...
Methyl alcohol	.273	..	...

extent to which this occurs and the actual values for the sorption by Smith's "Air C" charcoal for $p/p_s = 0.5$ at 120 and 205° are compared in Table XV.

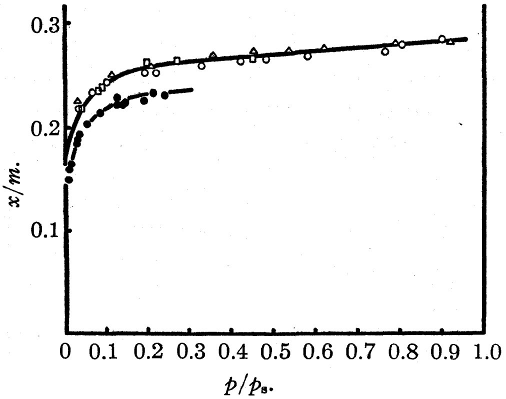

Fig. 5.—Sorption of heptane by "**Air** C" charcoal (H. P.L.). A, Expt. 17, 120°; O, Expt. 22,120"; ○, Expt. 24, 120°; ●, Expt. 24, 205'.

The ratio for acetic acid was 1.21 for Bakr's "Air and Vacuum B" and 1.08 for Wright's "Steam D" charcoal. For methyl alcohol between 40 and 120° the ratio is 1.24.

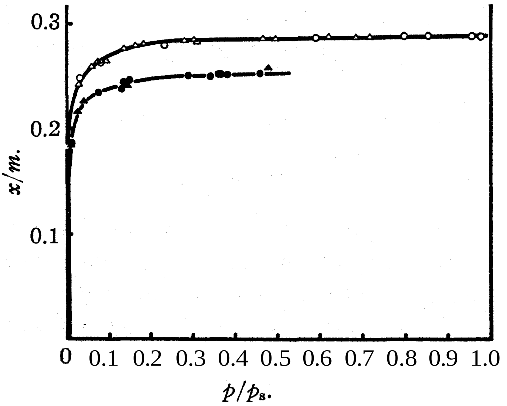

Fig. 6.—Sorption of octane by "Air C" charcoal (H. P. L.). ○, Expt. 12, 120°; ●, Expt. 12, 205°; A, Expt. 13, 120°; A, Expt. 13, 205°.

Bakr and McBain[11] observed that with Kahlbaum's (unactivated) sugar charcoal and their particular technique the weight of acetic acid which could be sorbed by 1 g. of charcoal was 1.34 times greater than the weight of toluene which could be sorbed under the same conditions. It is in-

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[11] A. M. **Bakr** and J. W. **McBain**, THIS JOURNAL, 46, 2718 (1924).

teresting to note that in the experiments here recorded for activated sugar charcoals, "Air C," Wright's "Steam D" and "Air and Vacuum B," the

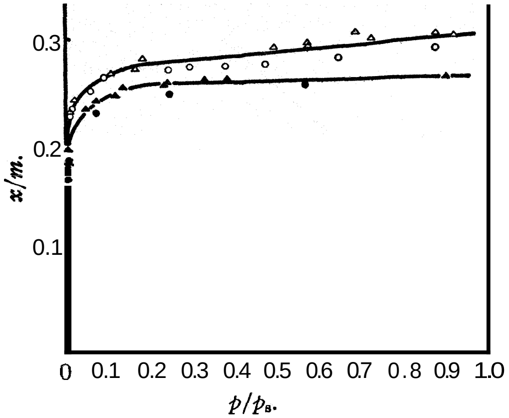

Fig. 7.—Sorption of decane by "Air C" charcoal (H. P. I,.). O, **Expt. 16,** 120°; ●, **Expt.** 16,205'; **A, Expt.** 20, 120°; **A, Expt.** 20, 205'.

corresponding ratios for acetic acid and toluene are 1.35, **1.35** and 1.36, respectively. Such comparisons can only be made when the vacuum technique for both cases is precisely similar. Likewise, in the present experi-

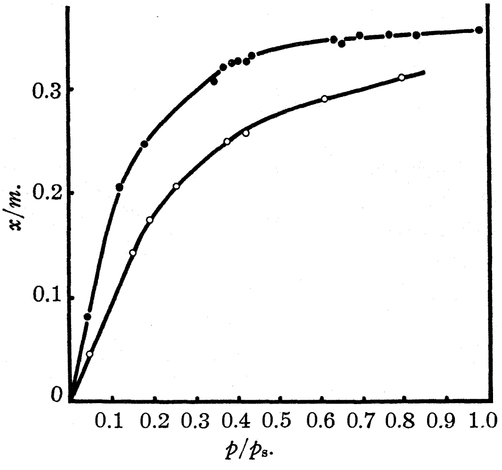

Fig. 8.—Sorption of methyl alcohol by "Air C" charcoal (H. P. I,.). O, **Expt.** 25,120'; ●, **Expt.** 25, 40°.

ments (H. P. L.), the relative maximum amounts which can be sorbed by "Air and Vacuum B," Wright's "Steam D" and "Air C" charcoals are in the proportion of 1 to 1.04 and 2.38, respectively, for acetic acid and 1 to

1.03 and 2.37, respectively, for toluene. Activation thus exerts similar effects upon the sorption of both substances.

Our interpretation of sorption data with charcoal is that there is just room at each temperature within the charcoal for the close packed molecules to lie each in contact with carbon, fitting in as best they may in the open structure and incomplete composite lattices of the charcoal. We should not describe the temperature effect in terms of expansion of a liquid, compressed or otherwise, nor of a compressed atmosphere.

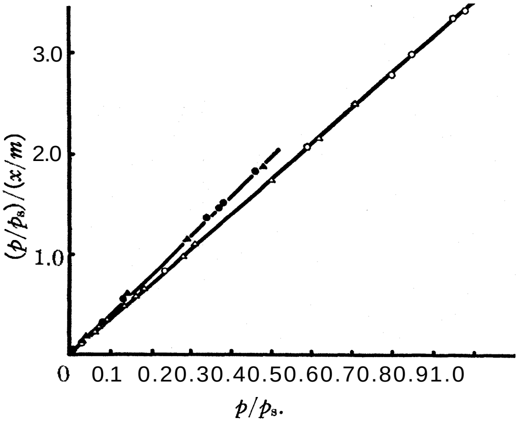

Fig. 9.—Langmuir graph, octane data of H. P. L., using "Air C" charcoal. O, Expt. 12, 120°; ●, Expt. 12, 205°; A, Expt. 13, 120°; A, Expt. 13, 205°.

It is obvious that, if this conception be true, E. H. du Bois Reymond's term "adsorption" is as much of a misnomer as when applied to the molecules of water in a zeolite or the sodium or calcium atoms in a water softener such as permutite. Nor can sorption by charcoal be described as solid solution, because this presupposes complete homogeneity. We have in another communication called this type of sorption, "persorption."

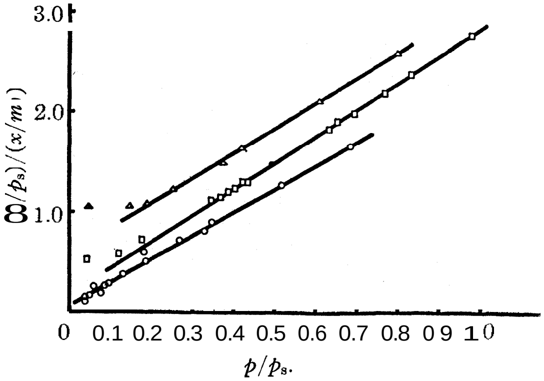

Fig. 10.—Langmuir graph for acetone and methyl alcohol, using "Air C" charcoal. O, P. F. C., acetone, Expt. 6, 120°; △, H. P. L., methyl alcohol, Expt. 25, 120°; a, H. P. L., methyl alcohol, Expt. 25, 40°.

The ordinary empirical sorption formula, $x/m = kp^{1/n}$, fails to represent such data as these. Its logarithmic graph, instead of being a single straight line, becomes a flat curve concave downward, changing rather suddenly into a nearly horizontal line at the upper range of pressure. The most adequate formula for representing the ranges here investigated is that of Langmuir, $x/m = abp/(1 + ap)$, which should yield straight lines in graphs such as are shown in Figs. 9 and 10, which exhibit the same data as Figs. 4, 6 and 8, although these differ greatly from each other. Similar straight lines were obtained in our previous communications,, including studies of sorption of nitrogen, nitrous oxide and ethylene up to sixty atmospheres. The only exception we have found is with methyl alcohol, for which there is a defect in sorption in part of the lower range of pressures. This may provisionally be attributed to the residual impurities which have been shown most greatly to affect this part of the isotherm. Acetone, like all the other substances, gives practically a straight line on the Langmuir diagram.

Inspection of the results with acetic acid shows that the results with different portions of a particular charcoal may be made reproducible. A close study of the data, as for example those for decane, shows that even with the mode of evaluation here employed, the time factor has not been wholly eliminated, although it is incomparably less than in experiments previously reported with less drastic procedures.

Conclusions

The thoroughness in evacuating and freeing activated charcoal from previously sorbed material, which is permitted by the use of the McBain–Bakr sorption balance in a sealed system, develops sorption isotherms of a new type in which nearly all the sorption occurs at very low pressures.

In some cases over the whole of the remaining range of higher pressures, there is practically no further sorption. The more drastic the preliminary purification of the carbon, the nearer is the approach to this type, which, therefore, appears to represent the true characteristic behavior of a pure vapor when sorbed by pure carbon. Data such as ours are adequately represented only by the Langmuir formula.

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[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE POISONING ACTION OF WATER VAPOR AT HIGH PRESSURE ON IRON SYNTHETIC AMMONIA CATALYSTS

BY P. H. EMMETT AND STEPHEN BRUNAUER

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Introduction

The mechanism of the poisoning action of water vapor and of oxygen on pure and promoted iron catalysts was first studied by Almquist and Black.[1] They found that during the passage of mixtures of 3:1 hydrogen–nitrogen gas containing 0.016% or more water vapor over iron synthetic ammonia catalysts at 444°, appreciable amounts of oxygen were retained by the catalysts. Concurrently with the addition of this oxygen, the activity of the catalyst toward the synthesis of ammonia at one atmosphere pressure decreased. According to an extrapolation from the data of Eastman and Evans,[2] ordinary massive iron is not oxidized at this temperature by a water vapor–hydrogen mixture containing less than about 16% of water vapor. Accordingly, Almquist[3] concluded that oxygen taken up by the catalyst was in the form of a "surface oxide" resulting from the interaction of water vapor and the active surface iron atoms of high degree of unsaturation. By assuming that this oxide phase was the same as ordinary Fe_3O_4, he calculated that the difference in free energy between crystalline iron and the more active surface iron atoms is of the order of 12,000 calories per gram atom of iron. By making the further assumptions that the active atoms taking part in the surface oxide formation are also responsible for most of the ammonia synthesis, and that the combination of active iron atoms and oxygen atoms occurs in the ratio of one to one, he calculated that in the pure iron catalyst approximately one atom out of every two thousand is active toward ammonia synthesis, whereas in the iron catalysts promoted with aluminum one atom out of every two hundred is active.

The investigations described in this paper were undertaken for the purpose of extending the experiments of Almquist and Black to higher pressures. It is well known that the activity of a synthetic ammonia catalyst at high pressures cannot be predicted from its activity at one atmosphere, since the variation of the efficiency of a catalyst with pressure is different for each individual catalyst. As Almquist and Black pointed out, catalyst 921, an iron catalyst promoted with aluminum, is slightly more active at atmospheric pressure than catalyst 922, an iron catalyst promoted with both Al_2O_3 and K_2O, whereas at 100 atmospheres' pressure

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[1] Almquist and Black, THIS JOURNAL, 48, 2814 (1926).

[2] Eastman and Evans, ibid., 46,896 (1924).

[3] Almquist, *ibid.*, 48, 2820 (1926).

catalyst 922 is 50% more active than catalyst 921. Furthermore, it was observed in the previous poisoning work that the higher the activity of a catalyst at one atmosphere pressure on pure 3:1 gas, the greater the amount of surface oxide it is capable of picking up. Accordingly, it seemed that a comparison of the activities of several synthetic ammonia catalysts with the amounts of oxide formed in the presence of small percentages of water vapor in the hydrogen–nitrogen mixture at pressures up to 100 atmospheres would probably give some clue to the cause of the pressure coefficients in synthetic ammonia catalysts and would at the same time furnish additional information concerning the mechanism of the poisoning of iron catalysts by water vapor.

Apparatus

The apparatus used in the present experiments was designed to permit the passage, at a definite rate, of a known mixture of hydrogen, nitrogen, and water vapor over an activated synthetic ammonia catalyst at pressures between 1 and 100 atmospheres, and to obtain a complete analysis of the gases leaving the catalyst bomb. The difference between the water content of the influent and effluent gases has been considered to be a measure of the amount of water vapor reacting with the catalyst to form oxide.

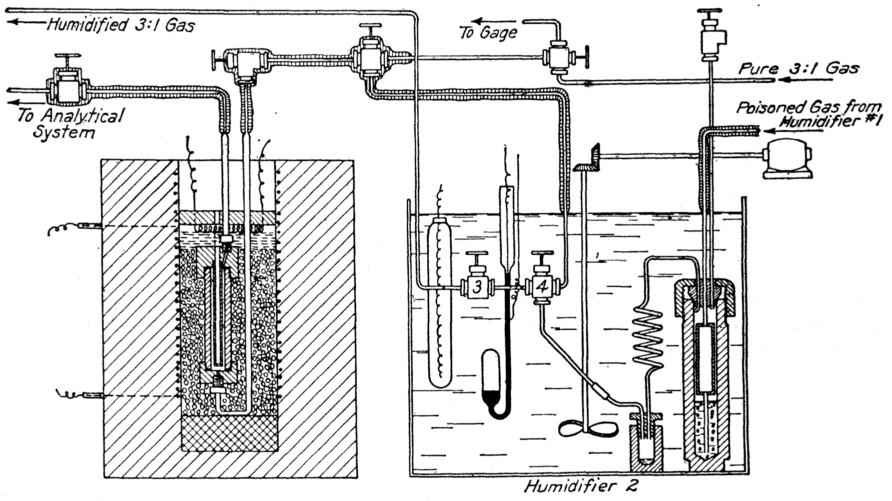

Fig. 1.

The high pressure supply of 3:1 hydrogen–nitrogen gas was the same as that described in a number of publications from this Laboratory.[4] It was obtained by burning electrolytic hydrogen in a limited supply of air and compressing the resulting 3:1 gas mixture to 2500 or 3000 lb. By means of an automatic pressure regulate working in conjunction with an especially constructed pressure gage, any pressure between 30 and 100 atmospheres could be automatically maintained in the reaction bomb. The compressed gas mixture was freed of oxygen and carbon monoxide by passage over hot cop-

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Larson and Dodge, THIS JOURNAL, 45,2918 (1923).

[5] Larson and Karrer, *J. Ind. Eng.* Chem., 14, 1012 (1922).

per and hot nickel, respectively. It was then passed through an ice-bath for condensing most of the water, and finally dried by passage through a series of five bombs, the first two filled with soda lime, the next with anhydrous aluminum oxide gel and the last two with pieces of fused potassium hydroxide. The resulting gas contained only a few thousandths of a per cent. of water vapor and was checked for purity during the runs by passage over a pilot catalyst maintained at 444° by a bath of boiling sulfur.

From the purifiers, the 3:1 gas mixture passed into the apparatus shown in Fig. 1. By appropriate adjustment of valves, the pure dry gas could be sent either directly into the reaction bomb or through a trap into humidifier No. 1 (not shown in diagram), then into humidifier No. 2 and finally into the reaction bomb. The first of the two humidifiers was maintained at a temperature approximately 5° above that of the final humidifier. Temperature was maintained accurately in the latter to ±0.1°. Calibration runs indicated that complete humidification was obtained without attendant mist or spray formation.

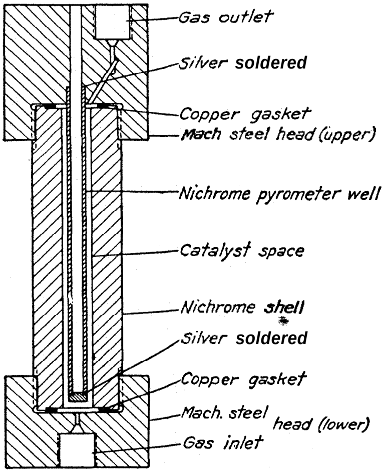

Fig. 2.

The reaction bomb containing the catalyst is shown in Fig. 2. It was made of nichrome steel and was so designed as to permit the plating of the 16-mesh catalyst particles in a thin layer around a thermocouple well extending the full length of the bomb. Uniform external heating was obtained by packing the bomb with mossy copper into an electric furnace as shown in Fig. 1. The furnace contained an alundum core wound with nichrome wire and packed with a thick layer of "85% Magnesia" into an outer iron jacket. An auxiliary heater on the top of the furnace permitted the temperature gradient along the length of the furnace to be kept down to 3°. The temperature of the bomb was measured by an alumel–chromel thermocouple in conjunction with a Leeds and Northrup type K potentiometer and was maintained by hand regulation of the furnace to ±3° during a particular run. All other temperatures were read by thermometers checked against calibrated Bureau of Standards thermometers.

Procedure

At the beginning of a series of runs the catalyst bomb containing approximately 5.3 cc. of the desired catalyst was packed into the electric furnace and connected as shown in Fig. 1. The catalyst was reduced with a 3:1 hydrogen–nitrogen mixture at one atmosphere pressure for a number of hours at temperatures below 450°. It was finally brought to a steady reactive state toward ammonia synthesis at 100 atmospheres' pressure.

In each run, at a given time, t_0, poisoned gas from the humidifiers was substituted for the stream of pure gas that had been passing through the reaction bomb at the desired temperature and pressure. At the same time, a stream of the high pressure humidified gas was reduced to one atmosphere by valve 3, and passed through a weighed phosphorus pentoxide tube into a wet gas meter. This blank run was used as a check on the water vapor content of the poisoned gas. The passage of poisoned gas through the catalyst bomb was continued until analysis of the exit gas showed a constant percentage of ammonia. Both the blank and poisoning runs were then terminated simultaneously. The rate of gas passage was regulated to 5000 space velocity. The total volume of gas passing the reaction bomb was measured by a carefully calibrated and frequently checked wet gas meter. The exit gas from the bomb passed first through an apparatus for quantitatively determining the water vapor, then through a series of boric acid solutions for absorbing all of the ammonia and finally into a wet gas meter. At frequent intervals during each run the following data were recorded: the temperature of the water in each of the gas meters, the barometric pressure, the temperature of the final humidifier, the readings of the gas meters and the concentration of ammonia in the exit gas. The method adopted in the present experiment for analyzing a stream of gas for water vapor in the presence of large concentrations of ammonia seems of sufficient general interest to merit a rather detailed description.

Method for the Determination of Small Concentrations of Water Vapor in a Gas Containing Large Percentages of NH_3.—Ammonia reacts with most of the usual chemical drying agents including phosphorus pentoxide, dehydrite and calcium chloride. Consequently none of these substances is suitable as a drying material for determining small quantities of water vapor in a gas containing large and variable amounts of ammonia. As pointed out by Almquist and Black,' fused potassium hydroxide will take up water vapor without absorbing ammonia. However, for the present experiments the quantities of water vapor were so small that it was found impracticable to prepare tubes of fused potassium hydroxide that would quantitatively absorb all of the water vapor during the hour run and would, at the same time, permit the free passage of the desired flow of approximately 420 cc. of gas per minute. Consequently, U-tubes filled with 20-mesh fused and crushed potassium hydroxide particles were used only for removing the water from the few samples of gas analyzed for ammonia during each run. The main portion of the exit gases was analyzed for water vapor by the apparatus shown in Pig. **3.**

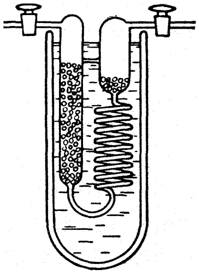

Fig. 3.

A U-tube filled with glass beads was immersed in an alcohol–carbon dioxide bath at −78°. In each run the first of the gas passing through the tube contained sufficient ammonia to permit the condensation of a considerable amount of liquid ammonia in the bottom of the bead tube. The water vapor of the gas passing into the U-tube was found to be completely absorbed by the liquid ammonia. At the end of each run, the liquid ammonia remaining in the U-tube was removed by flushing with a few liters of pure dry 3:1 hydrogen–nitrogen gas. The tube was permitted to come to room temperature, wiped carefully with alcohol and weighed. The slight excess gas pressure in the tube was then released, care being taken not to blow any liquid particles of water out of the tube. After being reweighed, the bead tube was flushed free of all adsorbed and dissolved ammonia. This latter was collected in distilled water and titrated against 0.01 *N* sulfuric acid, using sodium alizarin sulfonate as indicator. From these data, the total weight of water passing the catalyst could readily be obtained. Blank runs in which as much as 500 mg. of moisture was passed into the tube showed quantitative absorption of the water vapor.

Experimental Results

Data were obtained on fresh samples of three catalysts designated in the present work as 922, 921 and 918 and identical with the similarly numbered catalysts used by Almquist and Black. All of the catalysts consisted essentially of metallic iron. Catalyst 921 contained 1.31% Al_2O_3; catalyst 922 was promoted with 1.05% Al_2O_3 and 0.25% K_2O; catalyst 918 was a sample of pure iron containing no promoter. All were obtained by reducing with 3:1 hydrogen–nitrogen gas Fe_3O_4 prepared by a fusion method already described.[6] Their activities as ammonia catalysts under various temperature and pressure conditions have been described by Almquist and Crittenden.[7]

The manner in which the percentage of ammonia formed by a catalyst varies with time during a poisoning experiment is illustrated in Fig. 4. The curves are of the same general type as those shown by Almquist and Black for one atmosphere poisoning. A definite and constant activity toward the catalytic synthesis of ammonia is reached within a few minutes after the change from pure to poisoned gas. The constancy of this level was checked in several experiments by running on poisoned gas for as long as two hours without obtaining any indication of a further decrease in the activity of the catalyst. The activity of a promoted catalyst returns practically to its original value within less than an hour after changing from poisoned to pure gas. However, a definite decrease in the activity of the promoted catalysts on repeated poisoning and reduction could be detected. Thus in the course of twelve poisoning runs of approximately one hour duration each and the reduction of the oxide formed, the doubly promoted catalyst 922 gradually decreased from an activity corresponding to 12.5% ammonia produced at 100 atm., 450° and 5000 space velocity to one corresponding to 9.96% ammonia produced under similar conditions. The singly promoted catalyst 921 also became less active though not so rapidly as catalyst 922; during eighteen poisoning runs it decreased

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[6] Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

[7] Almquist and Crittenden, *ibid.*, **18**, 1307 (1926).

from a conversion of 8.88% ammonia to one of 7.56% ammonia. The catalytic activity on poisoned gas also decreased. In the above-mentioned runs on catalyst 922 in the presence of 0.32% water vapor, the percentage of ammonia in the exit gas dropped from the value 2.3 to 1.34, whereas that produced by catalyst 921 decreased from 2.92 to 2.27% ammonia. This decrease in activity with long exposure to poisoned gas is probably a manifestation of the same property by virtue of which a doubly promoted catalyst is found to be much less active if reduced at 100 atmospheres' pressure than if reduced at one atmosphere, the high partial pressure of water vapor present during reduction acting effectively the same as a long-continued poisoning run.

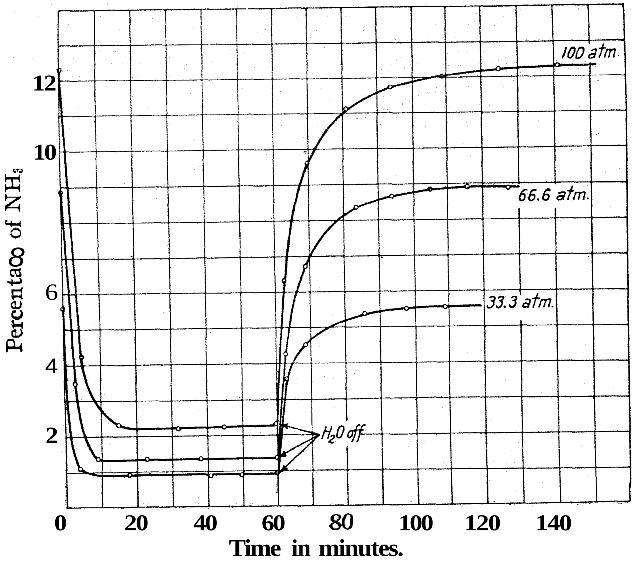

Fig. 4.—Effect of 0.32% water vapor on the activity of catalyst 922 at various pressures.

In Fig. 5 are shown curves based upon measurements made at 33, 66 and 100 atmospheres, representing the change of efficiency with pressure for catalysts 921 and 922, both when operating on pure and on poisoned gas. It is evident that the presence of 0.32% water vapor caused the doubly promoted catalyst 922 to decrease by not only a larger percentage of its activity than did the singly promoted catalyst 921, but to an actually lower level than catalyst 921. However, since the slope of the pressure efficiency curve for catalyst 922 is based upon an average of several successive runs during which the catalytic activity changed materially, no significance can be attached to the apparent similarity between the slopes of the pressure efficiency curves on poisoned gas runs of catalysts **921** and **922.**

Unfortunately, the activity of the pure iron catalyst 918 decreased very rapidly. It was possible to make only two 100-atmosphere poisoning runs on a given charge of the catalyst and even in these the catalyst was effecting only a 1% conversion to ammonia at 100 atmospheres, 450° and 5000 space velocity.

The results of the poisoning experiments are summarized in Table I. Here are shown the average amounts of oxide formed on the 5 cc. of catalyst used under the different experimental conditions encountered. The average of several blank runs is also shown. During these latter runs the procedure of the regular poisoning experiments was followed, though no catalyst was placed in the reaction bomb. All blank values were within the range —0.6 mg. and $0.4 mg. There are also shown a few runs at temperatures other than 450°.

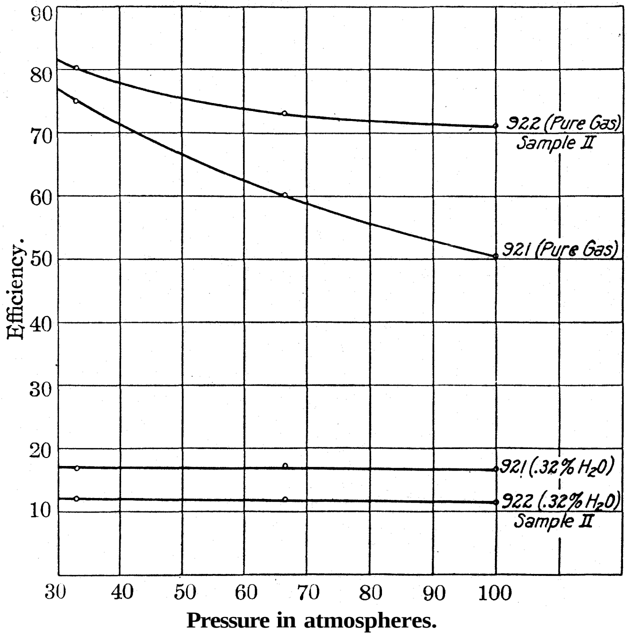

Fig. 5.—Variation with pressure of the efficiency of singly and doubly promoted iron catalysts on pure and poisoned 3:1 gas.

It is estimated that each individual reading might involve an error as large as ±3 mg. The values obtained as an average of several readings are, however, more reliable. The maximum deviation from the mean in the four blank runs was 0.6 mg.; in the two runs on catalyst 918 it was 0.8 mg.

The results recorded in Table I seem to warrant the following conclusions.

1. The amount of oxygen picked up by a particular catalyst at 450° is approximately proportional to the $\sqrt{P_{H_2O}}/\sqrt{P_{H_2}}$ throughout the range of P_{H_2O} and P_{H_2} values used in the present experiments.
2. At high pressure promoted synthetic ammonia catalysts take up much more oxygen than do pure iron catalysts. It will be noted that the experimental errors were too large to permit a decision as to whether the singly or doubly promoted catalyst picked up the more oxygen.
3. The temperature coefficient of the surface oxide formation is small. Only two runs were made at 400 and one at 500°. The sign of the temperature coefficient is accordingly uncertain.
4. The oxygen content of the catalyst is present as oxide and not as "adsorbed" water molecules, since the number of the latter would doubtless be a function of the absolute P_{H_2O} and not of $\sqrt{P_{H_2O}/P_{H_2}}$.

TABLE I

SURFACE OXIDE RETAINED BY VARIOUS CATALYSTS

5000 Space Velocity

Catalyst	Temp., °C.	H_2O in 3:1 gas, %	Press., (atm. abs.)	No. of expts. averaged	Mg. of H_2O retained by catalyst as oxide	Ratio of total *Fe* atoms to active Fe atoms Present expts., 1–100 atm.	1 atmosphere. Almquist and Black
918	450	0.34	100.0	2	0.3	11,000	1680
921	450	.08	100.0	1	4.1	810	404
	450	.33	100.0	8	11.3	294	218
	450	.48	100.0	1	13.1	253	183
	450	.33	66.6	2	10.1	328	218
	450	.32	33.3	2	7.5	443	218
	400	.33	100.0	2	7.3	455	...
	470	.33	100.0	1	8.0	415	...
	500	.33	100.0	1	10.4	319	...
922	450	.08	100.0	1	5.0	636	441
Sample I	450	.33	100.0	6	12.3	259	253
	450	.32	66.6	3	11.9	267	253
	450	.32	33.3	2	10.1	315	253
922	450	.08	100.0	1	5.3	590	441
Sample II	450	.33	100.0	4(1)[a]	10.6(8.0)[a]	295(391)[a]	253
	450	.48	100.0	1	13.7	228	...
	450	1.23	33.3	1	219	143	...
	450	0.33	1.0	2(3)[a]	7.0(8.2)[a]	447(381)[a]	253
Blank runs	450	.32	100.0	4	−0.2	...	...

[a] In a number of runs the oxide retained by the catalyst was also determined by reduction. The quantity of oxide so determined is given in parentheses.

Discussion

The oxide formed on the promoted iron catalysts in the present experiments is believed to be due predominantly to the production of a surface oxide only and not to the formation of solid solutions of oxygen or iron oxide in iron. The evidence in favor of this conclusion is two-fold. In the first place, the rate of formation and of removal of a large part of the oxide in the poisoning experiments is very rapid. Experiments showed, in fact, that most of the oxide was formed during the first seven or eight minutes after the initial contact of the poison with the catalyst and removed in a similar period after the replacing of the poisoned gas by pure gas. No oxide was formed during that period in which the exit ammonia value had attained the constant low value. This is certainly not characteristic of the manner in which water would distribute itself throughout the mass of catalyst as a uniform solution of oxygen or iron oxide in iron. In the second place, the amount of oxide is some ten-fold greater in the case of the promoted catalysts than in the case of pure iron catalysts, in spite of the fact that the rate of reduction and hence presumably also of oxidation of the pure iron at 450° is several fold greater than that of promoted iron. Were the oxide present in the form of solid solution, it would seem logical to expect the pure iron sample to reach saturation more rapidly than the promoted iron samples, and to retain an equal amount of oxygen.

It is interesting to note that the 0.1% surface oxide fprmed on doubly promoted catalysts in the present experiments at 450° with 0.32% water vapor is about the same as reported recently by Krings and Kempkens[8] to be formed at 700° by the exposure of pure iron samples to a mixture of steam and hydrogen containing approximately 30% water vapor, a percentage slightly smaller than is necessary to form the stable ferrous oxide. In view of the fact that the ten-fold greater $\sqrt{P_{H_2O}}$ in their experiments as compared to ours would tend to compensate for their using pure iron at 700° in contrast to promoted iron at 450°, it seems very probable that the 0.1% oxygen content reported by them to be the maximum amount of oxide formed on the iron samples without converting them partially to the ferrous oxide phase is a surface oxide.

In Table I are compared the ratios of total iron atoms to iron atoms picking up oxygen atoms under the various conditions of pressure and water vapor concentration used in the present experiments. It is here assumed that no more than one oxygen atom is picked up by a single iron atom. The ratios similarly calculated from the work of Almquist and Black for one atmosphere poisoning experiments are shown in the same table. Considering the difficulties involved in the oxide determination in the high pressure experiments, the agreement is satisfactory.

Almquist and Black conclude that the percentage of ammonia obtained in their experiments is inversely proportional to the oxide content of the catalyst. Furthermore, they point out that the oxide content of a particular catalyst varies approximately as the square root of the partial pressure of water vapor to which it is exposed. If these statements are true, it follows that at any given temperature and pressure the product of

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[8] Krings and Kempkens, *Z. anorg. allgem. Chem.*, 183, 225 (1929).

the percentage of ammonia and either the oxide content of the catalyst or the square root of the partial pressure of water vapor must be a constant. In Table II such products have been calculated both for the poisoning results of Almquist and Black and for our own high pressure results.

TABLE II

VARIATION OF CATALYTIC ACTIVITY WITH WATER CONCENTRATION

Catalyst	*Pressure*, atm.	P_{H_2O}, atm.	*Mg. of* H_2O *retained* as *oxide* = X	% NH_3	$K = (\sqrt{(P_{H_2O})}) \times (\% NH_3)$	$K' = (X) \times (\% NH_3)$
921	1	0.0004	4.8	0.205	0.00410	0.98
	1	.0008	6.6	.170	.00481	1.12
	1	.0016	9.4	.120	.00480	1.13
	1	.0032	12.2	.093	.00526	1.13
	1	.0048	14.5	.075	.00519	1.11
	100	.08	4.1	4.40	1.24	18.1
	100	.33	11.3	2.45	1.41	27.7
	100	.48	13.1	2.16	1.50	28.3
922	1	.0008	6.1	0.110	0.00311	0.67
	1	.0032	10.7	0.060	.00339	0.64
Sample I	100	.08	5.0	2.10	.60	10.5
922	100	.33	12.3	1.10	.63	13.5
Sample II	100	.08	5.3	2.30	.65	12.2
922	100	.33	10.6	1.34	.77	14.2
	100	.48	13.7	0.97	.67	13.3

Since deviations from constant values do not exceed the experimental errors, the results may be significant. It does not seem desirable to attempt to construct an ad *hoc* explanation to account for this peculiar relationship, for no reliable kinetic data have yet been obtained to account for the rate of synthesis of ammonia either at high or low pressures. It may be of interest to point out, however, that if the rate of ammonia formation is assumed proportional to some function of the hydrogen and nitrogen pressure, and inversely proportional both to the partial pressures of ammonia and partial pressures of water vapor as expressed by the equation

$$\frac{dP_{NH_3}}{dt} = \frac{kf_1(P_{N_2})\,f_2(P_{H_2})}{P_{NH_3}\,P_{H_2O}} \qquad (1)$$

then on integration, assuming the partial pressures of nitrogen and hydrogen constant during the short time of contact, one obtains the relationship $P_{NH_3} = k'\sqrt{t}/\sqrt{H_2O}$, in agreement with the results shown in Table II. Equation 1 is also in accord with the known inhibiting action of ammonia on the rate of synthesis.[9] It is intended, of course, to apply over only a limited range of partial pressures of water vapor. Such an equation is consistent with the assumption that the surface atoms responsible for most of the ammonia synthesis are covered a large fraction of the time by either ammonia (or its resulting nitride) or water (or its resulting oxide).

[9] Benton, *Ind. Eng. Chem.*, 19,494 (1927).

The time during which such points would be free to participate in the synthesis of ammonia would then be inversely proportional both to the ammonia and water vapor partial pressures as expressed in the above equation. The known increase in oxide content of the surface with the partial pressure of water vapor would on this basis have to be accounted for by assuming that most of the oxide formed by the catalyst in the presence of high percentages of water vapor is located on other than those atoms active toward ammonia synthesis.

The excess free energy attributed by Almquist to the active surface atoms may be an important factor in the mechanism of ammonia synthesis. Frankenburger[10] has calculated that an excess free energy of 12,000 calories or more per gram atom of active iron would permit the formation of Fe_2N on the active iron atoms on the catalyst surface by a pressure of three or four atmospheres of nitrogen at 377°, assuming the dissociation pressure of Fe_2N to iron and nitrogen to be 50,000 atmospheres. It should be pointed out that the calculation of Frankenburger yields the above result only if one assumes one active iron atom for each nitrogen molecule reacting, as for example would be the case in the reaction

$$Fe_{(active)} + 3Fe + N_2 = 2Fe_2N$$

We have made similar calculations for the formation of surface Fe_4N at 444° using the recently determined[11] value for the dissociation pressure of Fe_4N into nitrogen and Fe of 5000 atmospheres. They show that to form surface Fe_4N according to the equation

$$Fe_{(active)} + 7Fe + N_2 = 2Fe_4N$$

pressures of 100 atmospheres of N_2 would be necessary when the active iron atoms concerned are those requiring 0.32% water vapor in 3:1 hydrogen–nitrogen gas to produce surface FeO. These results are consistent with the hypothesis advanced above that most of the oxide formed on the catalyst in the presence of high percentages of water vapor is located on other than those atoms active toward ammonia synthesis.

The reduction by hydrogen of surface Fe_2N formed by the reaction of nitrogen and surface iron atoms possessing sufficiently high excess free energies was advanced by Frankenburger as a possible mechanism of the catalytic synthesis of ammonia. This type of mechanism still seems very probable. However, in view of the results of the recent study[11] of the dissociation pressures of various iron nitrides, it is much more likely that the intermediate nitride is Fe_4N than Fe_2N.

Summary

The poisoning of synthetic ammonia catalysts by water vapor has been studied at 450° at pressures as high as 100 atmospheres and at various

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[10] Frankenburger, Ullmann, "Enzyklopadie der Technischen Chemie," Berlin, 1928, Vol. I, p. 393; also *Z.* Elektrochem., 34, 632 (1928).

[11] Emmett, Hendricks and Brunauer, THIS JOURNAL, 52, 1456 (1930).

partial pressures of water vapor between 0.08% and 0.64%. The amount of oxygen retained by the catalyst is proportional to $\sqrt{P_{H_2O}/P_{H_2}}$. Very active catalysts are capable of retaining more oxygen than less active catalysts. The poisoning of both doubly and singly promoted catalysts by water vapor is almost entirely reversible, though a slight permanent injury to the catalyst results. A probable mechanism of ammonia synthesis consists in the reduction by hydrogen of surface Fe_4N formed by the reaction of nitrogen molecules with surface iron atoms having average free energies sufficiently in excess of those of normal iron atoms.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

ACETAMIDE AND FORMAMIDE AS SOLVENTS FOR THE ELECTRODEPOSITION OF METALS

BY L. F. YNTEMA AND L. F. AUDRIETH

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The possible application of formamide and acetamide as suitable media for the electrodeposition of metals from solutions of their salts has been suggested by various investigators,[1] but has thus far been given only little attention. That such a suggestion is based upon excellent theoretical considerations becomes evident from a survey of the physical and chemical properties of both of these substances. That such an investigation is highly desirable becomes increasingly apparent from the stress which has recently been laid upon solvent chemistry and solvents, in particular, non-aqueous ones.

Their differentiation on the basis of their acidity and basicity, as developed by Conant and Hall,[2] has thus far been limited to a consideration of liquid ammonia, water, alcohol and glacial acetic acid. Ammonia is regarded as the most basic of these in view of its great tendency to unite with the hydrogen ion or proton to form the ammonated hydrogen ion, the ammonium ion. Consequently, ammonium salts[3] and acid amides[4] act as acids in liquid ammonia. Glacial acetic acid, because of its tendency to part with the proton more readily, is considered the most acidic of the four above-mentioned solvents. This characteristic of acetic acid accounts for two of its most unexpected properties. Certain acids, such as perchloric acid, have been found to be "stronger" in acetic acid solution than in a less acidic solvent, such as water. On the other hand, compounds such as acetamide, which are usually considered as neutral substances re-

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[1] Walden, *Z. physik. Chem.*, 46, 103 (1903); 54, 129 (1905); 55, 683 (1906).

[2] Conant and Hall, THIS JOURNAL, 49,3047, 3062 (1927).

[3] Franklin, *ibid.*, 27, 820 (1905); Browne and Houlehan, *ibid.*, 33, 1742 (1911).

[4] Franklin and co-workers, J. *Phys. Chem.*, 24, 81 (1920); THIS JOURNAL, 44, 486 (1922); 47, 1485 (1925).

ferred to water, yield well-defined salts and may even be titrated by acids when dissolved in glacial acetic acid. The character of substances may change completely depending upon the solvent employed. Semicarbazide and guanidine are usually regarded as aquo-bases, but from their behavior in liquid ammonia may also be looked upon as ammono-acids.

These considerations concerning the nature of ionizing solvents and the behavior of dissolved solutes therein are all the more striking since such long accepted criteria as the dielectric constants find no place in such a classification.

Formamide and Acetamide as Parent Solvents.—The substitution of an amide group for the hydroxyl radical in formic and acetic acid affects very profoundly the chemical and physical properties of these substances. The dielectric constants are increased, and, as preliminary studies show, the solvent properties are accentuated. Applying the criteria suggested by Conant and Hall, it is obvious that the acidity of the resulting amides as *solvents* is less than that of the acids from which they are derived. That formamide is the more acidic of the two amides in so far as their solvent action is concerned, is indicated by the following chemical evidence: (1) metallic derivatives of formamide are more stable toward water than those of acetamide; (2) addition products or solvates are formed much more readily by acetamide; (3) the acid addition products of acetamide are the more stable.

That both of these substances may be considered as parent solvents seems evident (1) from the solvent properties which both exhibit, (2) from the fact that both yield conducting solutions, (3) since they enter into combination with various inorganic salts to form solvates. A large number of compounds has been prepared which bear a relationship to these two substances analogous to that existing between the ordinary acids and bases, and water.

Like water, formamide is miscible in all proportions with alcohol, and only very slightly soluble in ether. Metallic derivatives have been prepared which are related to formamide in much the same way as the metallic hydroxides are to water, even in such respects as solubilities in the corresponding solvents. It is an excellent dissociating solvent.[5] The conductivities[6] of salts in it indicate a behavior which parallels that observed in water. Molar conductivities are decidedly smaller. A study of the conductance of sodium formamide in formamide indicates the fact that the anion, $HCONH^-$, common to both solvent and solute, possesses an unexpectedly low ionic mobility,[7] only about one-tenth of that of the hydroxyl

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[5] Walden, Bull. St. *Petersburg Acad. Sci.*, **1911**; *cf. C. A.*, *6*, **1394** (**1912**).

[6] Davis, Putnam and Jones, *J. Franklin Inst.*, **180**, **567** (**1915**); *cf. C. A.*, **10**, **305** (**1916**); Davis and Johnson, *Carnegie Inst. Wash. Pub.*, *260*, **71** (**1918**); *cf. C. A.*, **13**, **3061** (**1919**).

[7] Röhler, Z. *Elektrochem.*, **16**, **419** (**1910**).

ion at similar concentrations in water. Formamide, like water, acts upon bismuth and antimony halides to produce solvo-basic compounds.[8]

Investigations concerning acetamide have been very much more prolific and extensive. Metallic derivatives of acetamide have been found to be unstable in water, but quite stable in liquid ammonia. In this connection it is interesting to note that their character varies from that of salts in liquid ammonia, by virtue of the behavior of acetamide as an ammono-acid. to what may formally be considered as bases in the parent solvent. Numerous addition compounds of salts with acetamide have been prepared. Their existence is all the more marked, because of the limited number of such solvates formed by formamide. Formamide has a more powerful "amidohydrolytic" effect, as evidenced by the fact that many metallic salts react directly with the solvent to yield the corresponding metallic formamides. Although observations are, as yet, far too limited to permit of any definite generalization, it would seem that the tendency toward the formation of solvates decreases as the acidity of the solvent increases. Acetic acid apparently forms few solvates.

The behavior of both amides as cryoscopic solvents has been investigated by Bruni and Manuelli.[9] Both solvents react with various mercury salts to give solvo-basic products.

In consideration of the above facts and in line with a series of investigations which are being conducted in this Laboratory,[10] the suitability of these substances as solvents for the electrodeposition of metals was believed to have sufficient theoretical background to warrant the experimental procedure outlined below.

Electrodeposition of Metals from Solutions of Their Salts in Formamide.—A preliminary study of this subject was made by Röhler,[7] who employed the following compounds as electrolytes for the deposition of the respective cations: $Pb(NO_3)_2$, $PbCl_2$, $CuSO_4$, Cu_2Cl_2, ZnO, $ZnCl_2$, $SnCl_2$. Metallic anodes composed of the metals to be deposited were used. Anodic losses were invariably found to be greater than the weight of the metal deposited. These differences were ascribed to the solvolysis of the respective electrolytes with the resultant formation of the metallic formamides and free acid. Subsequent chemical action of the acid thus formed upon the metallic anodes was postulated to account for these discrepancies. The character of the discharged metals was found to be influenced by dissolved oxygen, and by exposure of the solution to air, necessitating the use of a closed electrolytic vessel. Röhler made unsuccessful attempts to

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[8] Bruni and Manuelli, *Z. Elektrochem.*, 11,554 (1905).

[9] Bruni and Manuelli, *ibid.*, 10, 601 (1904).

[10] The authors have studied the electrodeposition of metals from solutions of their salts in liquid ammonia and find that the results closely parallel those obtained in aqueous solution. The low temperature of deposition, however, does affect the character of the deposited metal.

deposit magnesium, aluminum, nickel, cobalt and iron from solutions of their respective chlorides.

These results were checked by the authors and supplemented by additional observations. For purposes of comparison all experiments were carried out at 100°. Fifteen cc. of formamide, purified by vacuum distillation, was placed in a closed electrolytic cell fitted with a platinum anode of one sq. cm. surface area and a copper cathode of varying size. A stirring device was employed to prevent impoverishment of the solution in the neighborhood of the electrodes. A 110-volt direct current, in series with a lamp-bank for variable resistance, was used. Results of typical runs are given in Table I.

TABLE I

ELECTRODEPOSITION OF METALS FROM FORMAMIDE AT 100°

Compound	Grams solute per 15 cc. solvent	Current density per sq. cm., amp.	Type of deposit
$Zn(CN)_2$	0.5	0.03	Adherent deposit. Continued electrolysis yielded spongy material
$Cd(CN)_2$	1.4	.02	Smooth, adherent deposit
$Pb(NO_3)_2$	3.0	.03	Non-adherent
		.06	Crystalline. Deposit is not uniform, but adheres only in spots
SnI_4	1.0	.04	Smooth, adherent
$(NH_4)_2SnCl_6$	2.0	.04	Excellent deposition
$Co(C_2H_3O_2)_2 \cdot 4H_2O$	2.0	.02	Poor deposit
		.05	Better deposition; adherent
$Ni(C_2H_3O_2)_2$	Satd.	.018	Fair, adherent deposit
$Ni(NH_3)_6Br_2$	2.0	.025	Good, adherent deposit

Where cyanides were used as electrolytes the odor of hydrogen cyanide soon became very apparent, indicative of the interaction of the solute with the solvent in accordance with the equation

$$Zn(CN)_2 + 2HCONH_2 = Zn(HCONH)_2 + 2HCN$$

This checks with previous observations made by Rohler, who noted that the solvolytic action of formamide upon dissolved metallic salts resulted in many cases in the formation of the free acid and the metallic formamide.

Cobalt and nickel plates were readily obtained. Even such complexes as nickel hexammino bromide were found to give very satisfactory results. The lesser stability of nickel complexes, noted previously from their behavior in aqueous solution, again differentiates these from the more stable cobalt complexes. In the hope that formamide might facilitate secondary dissociation of complex ions, such compounds as potassium cobaltic cyanide, potassium chromic chloride and potassium ferrocyanide were also investigated. No decisive results were obtained.[11]

[11] Preliminary experiments would seem to indicate that the stability of complex cations varies with the character of the solvent molecule which is associated. Franklin

Electrodeposition of Metals from Solutions of their Salts in Acetamide.—No work has been reported in which metals have been deposited from solutions of their compounds in fused acetamide. It has been shown by Bruni and Manuelli[g] that potassium iodide is almost completely dissociated in acetamide and that anhydrous manganous chloride, cobaltous chloride and cupric chloride are highly dissociated. When hydrated salts are dissolved, water is completely split off. Walker and Johnson[12] measured the electrical conductance of potassium chloride, iodide and cyanide and found them to be good conductors. Solutions of mercuric chloride were also found to conduct, but not as well as those of potassium chloride. Belladen[13] showed that the specific conductances of the halides of sodium, the chlorides of barium and calcium and potassium iodide bore the same general relationships to each other as in aqueous solution. In the case of cadmium iodide it was shown that stepwise dissociation took place with formation of the complex $CdI_4^{=}$ ion.

The electrolytic cell was the same as that described in the work with formamide. All the experiments were carried out at 100°. The acetamide was purified by vacuum distillation. Ten grams of acetamide and an amount of salt to make the solution approximately molar were used in each case. The average run was one or two minutes in duration.

TABLE II

ELECTRODEPOSITION OF METALS FROM ACETAMIDE AT 100°

Compound	Grams solute per 10 g. solvent	Current density per sq. cm., amp.	Type of deposit
$Zn(CN)_2$	0 117	0 05	Deposit localized
$Cd(CN)_2$	.164	03	Smooth, adherent
SnI_4	.624	.05	Smooth, bright
$(NH_4)_2SnCl_6$	.368 (not completely soluble)	.04	Smooth, bright, "treeing" after two minutes
$PbCl_2$	.278	,037	Spongy, non-adherent
$Ni(NH_3)_6Br_2$	.320	.03	Good, adherent; higher current densities give a black powdery deposit
$Co(NH_3)_5Cl_3$	.250		No deposit
$K_3Co(CN)_6$	.332		No deposit
$CoCl_2$	....	.02	Smooth deposit; higher current densities give a black powdery deposit
$TlC_2H_3O_2$	.263	.025	Some adherent deposit, marked "treeing"

has already shown that complex cations form much more readily in liquid ammonia than in water. Evidence already on hand in the chemical literature indicates that the more basic the donor molecule or solvent, the more stable the complex cation which is formed and the greater the tendency and the greater the number of such solvates probably capable of existence.

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[12] Walker and Johnson, J. Chem. *Soc.*, **87,** 1597 (1905).

[13] Belladen, *Gazz. chim. ital.*, 57,407 (1907).

The solution of the nickel salt was an intense green and that of the cobalt a deep blue. In every case there was some evolution of gas at the cathode.

A number of experiments were performed using hydrated salts of the metals given in Table II and unpurified acetamide that contained considerable water. The deposition was good in each case. When 1 cc. of water was added to the solution of $Zn(CN)_2$ in the purified acetamide, an excellent deposit was obtained.

Summary

1. Zinc, cadmium, lead, tin, cobalt and nickel were deposited electrolytically from solutions of their salts in formamide. Current densities were of the order of 0.02 to 0.04 amp. sq. cm. The temperature was 100°.
2. Zinc, cadmium, tin, lead, cobalt, nickel and thallium were deposited from solutions of their salts in acetamide, under similar conditions.
3. Metals higher than zinc in the electromotive series were not deposited from solutions in either solvent.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE VOLUMETRIC DETERMINATION OF THIOCYANATE WITH IODINE AND WITH IODATE

BY H. ARMIN PAGEL AND OLIVER C. AMES

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It has long been known that the quantitative oxidation of thiocyanate with iodine is extremely slow in neutral or in acid solution. The reaction is

$$NCS^- + 3I_2 + 4H_2O \longrightarrow SO_4^= + CN^- + 8H^+ + 6I^+ \qquad (A)$$

In slightly alkaline solution the above reaction is comparatively rapid, and a consecutive reaction occurs, $I_2 + CN^- \longrightarrow ICN + I^-$, giving the final quantitative relation

$$NCS^- + 4I_2 + 8OH^- \longrightarrow SO_4^= + 7I^- + 4H_2O + ICN \qquad (B)$$

Upon acidification the iodocyanogen again instantly and quantitatively reacts with iodide to form free iodine and cyanide. In the presence of a suitable buffer, Reaction B should go to completion rapidly with a moderate excess of iodine. Upon acidification the iodine in excess of that required for Reaction A may then be determined by back titration with standard thiosulfate, using starch as indicator.

During the past year we have investigated the iodimetric determination of zinc as zinc pyridine thiocyanate. Since pyridine interferes with the iodine titration it was hoped that a suitable non-volatile buffer might be found which would expel the pyridine on boiling and subsequently serve as a buffer for the oxidation reaction. Disodium hydrogen phosphate proved somewhat unsatisfactory, but borax served both purposes admirably. The suitability of borax as a buffer was studied with respect to time required for complete oxidation, the quantity of borax required and the minimum of excess iodine permissible for quantitative oxidation. Tables I and II show the results of this study. Table III shows the results obtained by using iodine liberated from standard iodate solution. While this work was in progress, Alfred Schwicker[1] published a paper in which he showed that ammonium borate is a very desirable buffer for the oxidation reaction. Schwicker gives a review of the proposed methods; therefore these will be omitted in this paper. Although ammonium borate would be unsuitable for our work, we have nevertheless very carefully checked his work and found it to be sound in principle, but certain details have undoubtedly been overlooked. Schwicker carried out his oxidation reactions using 5 to 10 cc. of 1 N ammonium borate with a considerable excess of free iodine, in total volumes apparently ranging from 20 to 90 cc. The amount of ammonium borate required for larger volumes and the means of judging the minimum excess of iodine when the quantity of thiocyanate is not known, are not given. We have found that 10 cc. of 1 N ammonium borate in 150 cc. of reaction mixture is sufficient, provided that 4 or 5 cc. of iodine is added in excess of the amount required for Reaction B. This excess can easily be determined with sufficient accuracy by adding 5 cc. of the iodine solution to a volume of water equal to that of the oxidation mixture and comparing the colors. Unless this precaution is taken, errors may arise due to coincidence, for if the calculated amount of iodine is added, the solution still remains very distinctly colored with free iodine, even at the end of three minutes (Schwicker states that one to two minutes is sufficient), giving all appearances of the reaction being complete. Upon acidifying and determining the excess iodine, the results may be nearly 2% low. Table IV shows the results of various amounts of excess iodine. Schwicker seems to have attempted the use of borax, and states that two hours is required for complete reaction. His experience is probably explained by Table I, since we likewise found that insufficient borax gave low results.

Materials and Apparatus

Bureau of Standards certified burets, pipets, and volumetric flasks were used in all precision measurements. A 25-cc. buret was used for the thiosulfate back titrations. The oxidation reactions were carried out in 250-cc. glass-stoppered pyrex Erlenmeyer flasks. Conductivity water prepared with a large, specially constructed all-pyrex still, was used throughout. Highest purity chemicals were used, except the borax ($Na_2B_4O_7\cdot 10H_2O$) which was Mallinckrodt C. P. grade. Samples of the recrystallized material, however, gave identical results. All standard solutions were kept in opaque bottles fitted with buret supports which permitted automatic filling by suction. To reduce errors, pipetted portions were used wherever possible. Eighteen liters of 0.1 *N* iodine (in 0.2 *N* potassium iodide) was prepared in a 20-liter bottle. This solution remained unusually constant in strength; nevertheless, it was standardized daily with arsenious oxide. The iodine solution was tested for iodate and cyanogen with negative results.

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[1] Alfred Schwicker, *Z. anal. Chem.*, 77, 278 (1929).

Approximately **0.1** *N* potassium thiocyanate was volumetrically standardized with **0.1** *N* silver nitrate, using ferric alum as indicator. The silver nitrate was gravimetrically standardized as silver chloride, both at the beginning of the work and again at the close. Likewise, the silver nitrate–thiocyanate ratio was redetermined, both with identical results. The different strengths of thiocyanate given in the tables were prepared by diluting measured amounts of the **0.1** N solution (actual **0.1010** molar or **6** X **0.1010** N as reducer in Reaction A). Standard potassium iodate solution was prepared by dissolving and diluting the calculated weight of the pure dried salt. The thiosulfate–iodine ratios were run under the same conditions that were present in the actual determinations—that is, the thiosulfate into the measured portion of iodine with corresponding acidity. It was noticed, however, that identical results were obtained in neutral solution. Starch indicator was used throughout. Temperature corrections for the standard solutions were taken into account.

Procedure

In all data given in Tables I and II, the iodine was added to pipetted portions of thiocyanate to which had been added the given amounts of borax dissolved in sufficient water to give a volume of 150 cc. during the oxidation reaction. After the addition of the iodine the containers were placed in a dark cupboard until the reaction was thought to be complete. The solution was then acidified with 10 cc. of 6 N hydrochloric acid and the excess iodine immediately titrated slowly with thiosulfate until almost colorless, before the starch indicator was added. The time given in these tables excludes the time required for adding the iodine. The normality of thiocyanate is given as reducer in acid solution (Reaction A). Iodine in excess to Reaction B is the difference between "iodine added" and $^4/_3$ times the "calcd. iodine."

TABLE I

EFFECT OF TIME AND THE QUANTITY OF BORAX

0.06733 *N* KSCN, cc.	Borax, g.	Time, min.	Iodine, 0.1008 *N* Added, cc.	Reduced, cc.	Calcd., cc.	Error, %
50	1	10	50.00	31.52	33.40	−5.6
50	3	10	49.52	33.26	33.40	−0.4
50	3	30	50.00	33.36	33.40	− .1
50	3	30	50.00	33.38	33.40	− .1
50	5	5	49.50	33.10	33.40	− .9
50	5	5	49.50	33.06	33.40	−1.0
50	5	10	49.50	33.37	33.40	−0.1
50	5	30	50.00	33.38	33.40	− .1
50	5	105	50.00	33.37	33.40	− .1
25	5	3	27.30	16.65	16.70	− .3
25	5	5	27.30	16.67	16.70	− .2
25	5	5	27.31	16.66	16.70	− .2
25	5	11	27.30	16.67	16.70	− .2
25	5	30	27.32	16.68	16.70	− .1

These results show that with 5 to 5.5-cc. excess iodine in a volume of 150 cc., it is necessary to use 5 g. of borax to insure complete reaction in ten minutes. With smaller amounts of thiocyanate the reaction is complete in five minutes but ten minutes is recommended in all cases. The following table shows the consistency of results obtained under the above conditions, and also that larger excess of iodine causes no error on long standing.

TABLE II

EXPERIMENTAL RESULTS

0 06733 N KSCN, cc.	Time, min.	Iodine, 0 1008 N				Error. %
		Added, cc.	Excess, cc.	Reduced, cc.	Cafcd., cc.	
50	10	49.52	5.0	33.38	33.40	− 0.1
50	10	40.50	5 0	33.39	33.40	.0
50	10	50 00	5 6	33 39	33 40	0
30	10	50 00	5 5	33 38	33.40	− .1
25	10	27.30	5 0	16.66	16.70	− .2
25	in	27.27	5 0	16.65	16.70	− .3
25	30	5000	27.7	16.66	16.70	− .2
(0.08657 *N*)						
25	45	40.00	11.3	21.45	21.47	− .1
50	30	65.00	7.7	42.86	42.94	− .2
50	30	65.00	7.7	42.89	42.94	− .1

A reference solution for judging the minimum excess of iodine should be prepared before starting the titration. A 5-cc. portion of iodine is added to a volume of water about equal to that of the solution to be titrated. During the early stages of the titration the iodine is reduced almost instantly, but later the color begins to fade slowly. At this point about 10 cc. more should be added. If at the end of two minutes the color is as dark or darker than that of the reference solution, the mixture is allowed to stand for at least eight minutes longer to insure complete oxidation; otherwise, more iodine is added until the proper excess is assured.

Instead of using 0.1 N iodine solution, the equivalent amount of 0.1 *N* iodate solution may be treated with 2 g. of potassium iodide followed by 10 cc. of 1 N hydrochloric acid. The thiocyanate solution containing 6 g. of borax is then added. The regular procedure as given for iodine is then followed. If the reaction mixture shows less than the required excess of iodine at the end of two minutes, a second portion of iodate is treated as above and the oxidation mixture is poured into the latter. It is advisable to add another gram of borax if a second portion of iodate is required.

Table III shows the accuracy of this modification.

TABLE III

RESULTS USING STANDARD IODATE

KSCN, cc.	Iodate, 0 1000 N			Error, %
	Added, cc.	Reduced, cc.	Calcd., cc.	
25 (0.06733 *N*)	25	16 81	16.83	− 0.1
50 (0 06733 *N*)	50	33.70	33.66	+ .1
50 (0.06733 *N*)	50	33.66	33.66	.0
25 (0.06060 *N*)	25	15.14	15.15	− .1
50 (0.06060 *N*)	(25 + 25)[a]	30.35	30.30	+ .2
50 (0.06060 *N*)	(25 + 25)[a]	30.33	30.30	+ .1

[a] Indicates a second portion of iodate.

Table IV shows the possible errors that may arise from coincidence, due to insufficient excess of iodine in following Schwicker's procedure. To 50-cc. portions of thiocyanate, the indicated amounts of iodine in excess for Reaction B were added and the mixture was diluted to 140 cc. Ten cc. of the ammonium borate (prepared according to Schwicker) was then added and the reaction allowed to proceed for two minutes before acidification, as Schwicker directs.

TABLE IV

Excess iodine, cc.......	0.0	0.0	0.2	0.5	2.0	4.0	4.0	5.0
Error, %.............	−1.7	−1.2	−0.9	−0.7	−0.3	−0.2	−0.2	−0.2

The possibility of this error has already been discussed in the introduction of this paper. The results were found to be quite accurate with very slight excess of iodine in the presence of 15 instead of 10 cc. of ammonium borate in a 150-cc. volume. A minimum of 4 to 5 cc. of excess iodine is, nevertheless, recommended.

Summary

It has been shown that under suitable conditions borax gives the proper alkalinity for the rapid volumetric determination of thiocyanate with iodine.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE EXISTENCE OF ELECTRONIC ISOMERS IN THE SOLID STATE AND IN SOLUTION. THE MAGNETIC SUSCEPTIBILITY OF $Sm_2(SO_4)_3 \cdot 8H_2O$ AND ITS VARIATION WITH THE TEMPERATURE

BY SIMON FREED

RECEIVED MARCH 26, 1930 PUBLISHED JULY 3, 1930

The quantum theory of Bohr and also the quantum mechanics[1] lead to the following relation connecting the paramagnetic susceptibility of a monatomic gas with the temperature

$$\chi = \frac{B^2g^2j(j+1)}{3RT} \qquad \text{I}^{2}$$

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[1] Sommerfeld, "Atombau," 4th ed., pp. 630–648; Van Vleck, *Phys. Rev.*, 31, 604 (1928).

[2] Formula I is the quantum analog to the formula derived by Langevin on the classical theory

$$\chi = M^2/3RT = C/T$$

where M is the magnetic moment generated by the unbalanced electrons in their orbits. $C = M^2/3R$ is known as Curie's constant. This formula expresses Curie's law, which states that the paramagnetic susceptibility is inversely proportional to the absolute temperature. The magnetic field is more effective in orienting the elementary magnets when the thermal agitation is less violent.

χ is the susceptibility per mole, B is the Bohr magneton per mole, *i. e.*, $Neh/4\pi mc$ (where N is Avogadro's number, e/m is the charge divided by the mass of an electron, h is Planck's constant, and c is the velocity of light), R is the gas constant per mole, T is the absolute temperature, j is the net angular momentum of the atom (*i.e.*, the vector sum of the spin moments of the electrons and their orbital moments), g is Landé's splitting factor, which indicates that a resultant between the magnetic moment due to the spins of the electrons and that due to their orbital moment has been taken.

The magnitudes g,j are determined by the characteristics of the electronic state of the atom (or atomic ion); that is, given the quantum number designating the net spin moment of the electrons, their net orbital moment, and the resultant angular momentum of the atom or ion as a whole, the values of g and j are known and the susceptibility is determined by **I.** Ordinarily one might expect that if several electronic configurations (electronic isomers) are present, the susceptibility of the mixture would be the sum of the partial susceptibilities of the two configurations as given by **I.** Van Vleck[3] has shown on the quantum mechanics that when more than one electronic form is present, another term must be added to **I.** This term is independent of the temperature (aside from the Boltzmann factors) and corresponds to the component of the magnetic moment perpendicular to the axis of the angular momentum. **I** takes only the parallel component into account. On the model employed by Van Vleck, the precession of the perpendicular component is identified with the frequency of the light attending the transition from one state to the other.

When the writer began these experiments the results derived from the quantum mechanics were not known. It appeared highly probable then that any marked deviation from Curie's law shown by atoms implied the presence of several electronic forms whose relative amounts were a function of the temperature,[4] for each electronic form has associated with it a magnetic moment. If Curie's constant, $M^2/3R$, varies with the temperature, it means that M is varying with the temperature. However, the magnetic moment cannot vary with the temperature since electronic motions are unaffected by thermal agitation. M must then be a composite magnetic moment which includes the concentrations of several forms having different magnetic moments and these relative concentrations are varying with the temperature.

The approach to this investigation was the following. Hund[5] and others in their elucidation of the spectra of complex atoms and ions showed how to

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[3] Van Vleck, *Phys. Rev.*, 31, 587 (1928).

[4] Laporte and Sommerfeld, *Z. physik*, 40,333 (1926).

[5] Hund, "Linienspectren und Periodisches System der Elemente," Julius Springer, Berlin, 1927.

predict the value of g and *j* from the number of electrons in the various shells of the atoms or ions. The electronic distribution employed was the one proposed by Stoner and by Main Smith in their work on the Periodic System. Having the values of g and *j*, Hund was in a position to calculate the magnetic moments and the susceptibilities of the ions of the rare earths in the gaseous state. Such data, however, do not exist, so he compared his results with the experimental values obtained with the ions in the solid state and with their solutions. The agreement was extraordinarily good for all ions except Sm^{+++} and Eu^{+++}, as may be seen from the table (I). Eu^{+++} being very rare and difficult to purify was at once suspected of being contaminated with paramagnetic impurities. Sm^{+++}, however, can be obtained very pure, as is attested by the accepted atomic weight, 150.43, and the good agreement in this value obtained by various experimenters. However, the susceptibility expected by Hund was much less than that actually found.

Materials

It was decided to measure the susceptibility of Sm^{+++} as in the salt $Sm_2(SO_4)_3 \cdot 8H_2O$. This salt is of such stability as to have warranted several investigators, in particular Urbain and Lacombe,[6] to base their determination of the atomic weight of samarium upon it. Their value of 150.46 for its atomic weight was practically identical with that obtained by Stewart and James,[7] who employed the ratio $SmCl_3$:Ag.

The $Sm_2(SO_4)_3 \cdot 8H_2O$ used in the present investigation was prepared from a sample of $Sm_2(C_2O_4)_3 \cdot 10H_2O$ of exceptional purity kindly furnished the writer by the late Professor C. James of the University of New Hampshire. It contained a trace of bismuth (the salts of bismuth are diamagnetic) used in its fractionation and this was removed with hydrogen sulfide after a procedure outlined by Professor James. The oxalate was again precipitated following the method of Stewart and James[7] in their determination of the atomic weight of samarium. The oxalate was converted into the oxide by ignition, and then into the chloride with redistilled hydrochloric acid. The crystals of $SmCl_3 \cdot 6H_2O$ obtained by evaporating the water were dissolved in alcohol and pure sulfuric acid was slowly added. The $Sm_2(SO_4)_3.8H_2O$ which precipitated was twice recrystallized from conductivity water and then dried in an electric oven at 80°. The sulfate was then put in an evacuated desiccator, together with its saturated solution, until it came to a practically constant weight. The sulfate was then removed and placed in a balance case, to avoid an excess of water being taken up by the pores of the sulfate. The weight became practically constant after several days. The loss of water from the pores was slight.

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[6] Urbain and Lacombe, *Compt. rend.*, 138, 1166 (1904).

[7] Stewart and James, THIS JOURNAL, **39,** 2605 (1917).

An analysis of the crystals showed that there were $8H_2O$ for every mole of $Sm_2(SO_4)_3$ to within 1%. As the analysis was not deemed more accurate than this uncertainty, the composition was taken as $Sm_2(SO_4)_3 \cdot 8H_2O$.

The susceptibility of the salts of trivalent samarium has been measured many times[5] and a rough attempt at determining its temperature coefficient was made by Zernike and James.[8] They gave as the fractional change in the susceptibility per degree change in temperature as $^1/_{1700}$ plus or minus 100%.

It was the aim in the present investigation to attain considerable precision and to achieve this a new sensitive method was devised for measuring susceptibilities at low temperatures.

Apparatus and Method

The best known method for measuring the susceptibilities of solids at low temperatures is that employed repeatedly at the Leiden Cryogenic Laboratory? After considerable experimentation that laboratory adopted the Gouy principle. The latter is employed as follows. A glass tube G with a glass partition P is placed in a magnetic field (MM are the pole pieces of the magnet) so that P is in the center of the pole gap. The portion of the tube above P is evacuated and that below P is filled with the crystals of the substance to be investigated. The extremities of G usually extend to regions where the magnetic field is of negligible intensity. The force which a magnetic field exerts on such a tube is

$$F = \tfrac{1}{2} AK(H^2 - H_o^2)$$

where F is the force, A is the net cross section of the substance, K is the susceptibility per unit volume, H is the magnetic field at the center of the pole gap and H_o is the intensity of the field at the end of the tube, in this case practically zero.

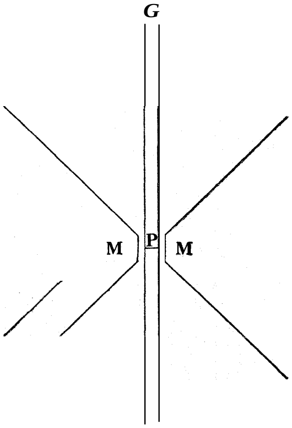

Fig. 1.

Reducing the temperature of the tube has generally been accomplished by putting it in contact with condensed gases such as boiling liquid nitrogen, liquid methane, etc. Intermediate temperatures have been obtained by reducing the pressure under which these liquids boiled. Such a reduction in pressure led to enclosing the entire apparatus in a vacuum-tight container and elaborate devices were resorted to for manipulating the enclosed system. The present method avoids these complications and permits the weighing of the tube to take place just as easily as if it were suspended in air at atmospheric pressure and at room temperature.

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[8] **Zernike** with C. James, THIS JOURNAL, **48**, 2827 (1926).

[9] Woltjer and Onnes, *Comm. Phys. Lab. Univ. Leiden,* No. 167C.

The glass tube *G* containing the $Sm_2(SO_4)_3 \cdot 8H_2O$ was suspended in the copper tube **A** (about 12 mm. in diameter and about 60 cm. long) from a stirrup of an analytical balance. The glass tube was surrounded by a gas at a known temperature with which it came in equilibrium. The gas streamed slowly through the small copper tube B of about 1 mm. bore into the bottom of **A** (there were actually two such tubes, B) and then out into the atmosphere at the upper end of **A.** The copper tubes B waved back and forth along the outside of **A** and not around it. *C* is the Dewar tube which contained the liquefied gases employed for cooling. It had a flattened constriction at D which fitted in between the pole pieces of the magnet. A rubber tube R fitted tightly around a wooden stopper F and also around the Dewar tube C. F was covered with a mixture of beeswax and rosin. TTT are double junction manganin–copper thermocouples on whose cold junctions there were fused little buttons of lead which obtruded slightly into **A.** The buttons were thermally and electrically insulated from the copper tube **A** by means of little wads of asbestos. The temperature calibration for these thermocouples was taken from the comparison of such couples with a hydrogen thermometer carried out in this Laboratory.[10]

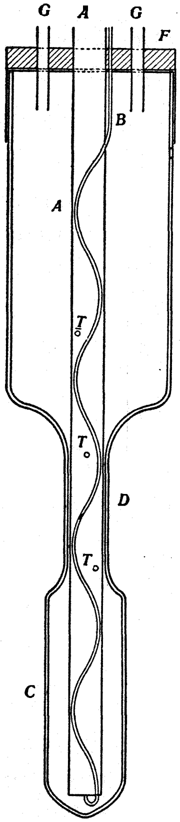

Fig. 2.

The thermocouples registered constant temperatures for hours at a time. A glass tube such as G having a thermocouple imbedded in salt was suspended in the copper tube **A** to see if the temperature of the thermocouples T actually read the temperature of the salt being studied. The temperature of the salt (at the temperature of liquid air) shown by the thermocouple was within less than 0.1° the same as that shown by the thermocouples T.

Sufficient regularity in the flow of the gas stream was achieved by means of a capillary tube about 0.001 mm. in diameter which delivered about **30** cc. of hydrogen gas per minute under normal conditions of temperature and pressure when the pressure at the hydrogen tank was about one atmosphere above the external pressure.

The upper 15 cm. of A is composed of German silver to lessen the heat leak and screwed to its upper end is a copper tube about 20 cm. long. The cold dry gas having passed through **A** has sufficient time to become warmed through the copper tube so that it leaves the apparatus above the dew point. Otherwise, moisture would condense upon the suspension and alter the weight. The suspension consists at its lower half of a very light brass chain. Its upper half is a silk fishing line, braided and lacquered in the usual manner. The brass chain is employed in the region of lowest temperature because the thermal contraction of brass is negligibly small and silk is used to minimize the heat leak to the chain. The same suspension was employed for all the runs including the calibration. Its length was adjusted at the beginning of the experimentation so that the glass partition P of the glass tube came in the center of the pole gap.

The operation is carried out as follows. Liquid air, for example, is introduced through *G* into C. A stream of dry hydrogen passing through B into **A** reaches the temperature of the liquid air and then comes in contact with the glass tube containing the $Sm_2(SO_4)_3 \cdot 8H_2O$ which is suspended in **A.** The gas finally passes out into the atmosphere through the top of **A.** To reduce the temperature of the $Sm_2(SO_4)_3 \cdot 8H_2O$,

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[10] Giauque, Buffington and Schulze, THIS JOURNAL, 49, 2343 (1927).

a large vacuum pump is connected to G and the temperature is lowered since the liquid air is now boiling under a lower pressure and in turn it further cools the hydrogen gas streaming through B. Now the $Sm_2(SO_4)_3 \cdot 8H_2O$ comes into thermal equilibrium with the colder hydrogen and the magnetic susceptibility is measured at this temperature.

The magnet was of the Weiss type employed in an earlier magnetic investigation.[11] The highest field used was about 19,000 gauss. The intensity of the field could be kept constant for considerable periods of time by a steady current from large storage batteries.

Method of Measurement

The tube A was magnetically calibrated at room temperature with a solution of nickel chloride (identical in purity with that employed in the investigation referred to).[11] The lower part of the tube A was filled with a solution of nickel chloride of known concentration. The change in weight suffered by the tube was observed as definite amperages were going through the coils of the magnet. (The diameter of the tube A had to be known and it was determined by measuring with a microscope the lengths of the tube which known weights of mercury would fill.)

The change in weight was plotted against the corresponding amperages. The solution of nickel chloride was then replaced by fine crystals of $Sm_2(SO_4)_3 \cdot 8H_2O$. The tube was now evacuated until the air between the crystals was at a pressure of about 20 mm. of mercury and it was then sealed off. Again the change in weight at fixed current strengths was observed and compared with the change experienced at the same current by the tube when it contained nickel chloride. Similar comparisons were made at the different temperatures. Equal currents imply equal field strengths. The method of calculation is as follows

$$F_s = \tfrac{1}{2} A_s K_s H^2$$
$$F_n = \tfrac{1}{2} A_n K_n H^2$$
$$\frac{F_s}{F_n} = \frac{A_s K_s}{A_n K_n}, \text{ or}$$

where F is the change in weight at the field strength H, A is the cross section of the material, K is the susceptibility per unit volume. s refers to $Sm_2(SO_4)_3 \cdot 8H_2O$; n refers to the solution of $NiCl_2$.

$$A_s K_s = A_n K_n \frac{F_s}{F_n} = \text{known magnitude} \qquad \text{(II)}$$

$$K_s = d_s \chi_s$$

where d is the density, χ is the susceptibility per gram

$$A_s = \frac{\text{grams } Sm_2(SO_4)_3 \cdot 8H_2O}{d \cdot l}$$

in the tube, where l is the length of the tube filled with the salt

Substituting in (II)

$$\frac{\text{grams } Sm_2(SO_4)_3 \cdot 8H_2O}{dl} \cdot d\chi_s = \text{known magnitude. Hence } \chi_s \text{ is known}$$

The susceptibility per mole is equal to the susceptibility per gram χs times the molecular weight of the sulfate octahydrate. To obtain the molal susceptibility of Sm^{+++} it is necessary to subtract the contribution (diamagnetic) of SO_4 and H_2O to the

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[11] Freed, THIS JOURNAL, 49, 2456 (1927).

susceptibility of the salt. The diamagnetic susceptibility (the susceptibility due to the balanced electrons) of Sm^{+++} was neglected. It is undoubtedly very small.[12]

TABLE I
MAGNET MOMENTS OF THE RARE EARTH IONS

Element	No. of 44 electrons[a]	Basic Level[b]	j	g	Calcd. no. of Weiss[c] magnetons	Observed no. of Weiss magnetons Cabrera	St. Meyer	Zernike and James	Decker
La^{+++}	0	^1S	0	0/0	diamag.	diamag.	diamag.		diamag.
Ce^{+++}	1	^2F	5/2	6/7	12.5	11.4	. .	11.7	10.5
Pr^{+++}	2	^3H	4	4/5	17.8	17.8	17.3	17.2	17.0
Nd^{+++}	3		9/2	8/11	17.8	18.0	17.5	17.4	17.1
Il^{+++}	4	^5J	4	3/5	13.4	. .	. .		. .
Sm^{+++}	5	^6H	5/2	2/7	4.2	8.0	7.0	7.6	8.1
Eu^{+++}	6	^7F	0	0/0	0	17.9	15.5	. .	19.7
Gd^{+++}	7	^8S	7/2	2	39.4	40.0	40.2	38.6	39.1
Tb^{+++}	8	^7F	6	3/2	48.3	47.1	44.8	46.3	485
Ds^{+++}	9	^6H	15/2	4/3	52.8	52.2	53 0	. .	54.0
Ho^{+++}	10	^5J	8	5/4	52.8	52.0	51.9	51 2	51.6
Er^{+++}	11	^4J	15/2	6/5	47.7	47.0	46.7	47.6	47.4
Tu^{+++}	12	^3H	6	7/6	37.6	35.6	37.5	. .	. .
Yb^{+++}	13	^2F	7/2	8/7	22.5	21.9	23	21.9	224
Lu^{+++}	14	^1S	0	0/0	0	diamag.	diamag.		6.1[d]

EXPLANATORY

[a] It is assumed that the only uncompleted electronic shell is 44. A few electronic assignments according to the Stoner–Main Smith procedure are given.

Electronic shell	1_1	2_1	22	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2
Electrons La^{+++}	2	2	6	2	6	10	2	6	10	0	2	6
Ce^{+++}	2	2	6	2	6	10	2	6	10	1	2	6
Gd^{+++}	2	2	6	2	6	10	2	6	10	7	2	6
Yb^{+++}	2	2	6	2	6	10	2	6	10	13	2	6
Lu^{+++}	2	2	6	2	6	10	2	6	10	14	2	6

The electrons in the completed shells have neutralized each other's magnetic moments. The resultant moment of the ion is then due to the incomplete shell which is finally filled in Lu^{+++} and this ion is actually found to be diamagnetic.

[b] The character of the basic spectroscopic level is obtained from the configurations indicated above by the Hund procedure. These levels with the accompanying **j** values give the net orbital moment, the net spin moment and the resultant angular momentum of all the electrons in the 44 shell and hence of the ion as a whole (since completed shells do not contribute to the moments).

[c] The Weiss magneton is an empirical unit of magnetic moment which has been of great service in magneto-chemistry. It is based upon the formula of Langevin and is equal to

$$B_{\text{Weiss}} = \frac{\sqrt{3R_X T}}{1126}.$$

The susceptibility of a substance obeying Curie's law is sufficient to express the moment in Weiss units. However, other magnitudes such as *j*, g, etc., must be known to

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[12] The diamagnetic susceptibility is proportional to the sum of the areas swept out by the electrons in their orbital motion. In the case of a triple charged ion, the electrons are so strongly attracted by high positive charges that the average radii of the electronic orbits are very small.

obtain the actual magnetic of the ion which is usually expressed in terms of the fundamental Bohr unit.

[d] Decker states that his Lu^{+++} was contaminated with Yb^{+++}.[13]

TABLE II

EXPERIMENTAL RESULTS

$Sm_2(SO_4)_3 \cdot 8H_2O$ in tube, 3.570 g. Cross section of inside of tube, 0.1032 cm. Length of tube filled with the sulfate, 18.03 cm. Concentration of $NiCl_2$ solution, 1.3660 M. Susceptibility per cc. of solution at 17.5°, 5.332 X 10^{-6}. Force on $Sm_2(SO_4)_3 \cdot 8H_2O$ at 290.6 °K. divided by the force on the $NiCl_2$ solution at 290.6 °K., 0.9134. Average deviation in 0.9134 for fields from 15,000 to 19,000 gauss is 0.26%

Temperature, °K.	Force on $Sm_2(SO_4)_3 \cdot 8H_2O$ as compared with that found at 290.6 °K. Ratio of forces	Average deviation for fields to 19,000, %
240.2	1.037	0.15
205.0	1.076	0.20
169.8	1.128	0.22
112.5	1.255	0.35
84.6	1.345	0.22
73.8	1.392	0.40
		Av., 0.26

TABLE III

SUSCEPTIBILITIES OF Sm^{+++} AT VARIOUS TEMPERATURES

Temperature, °K.	χ of $\frac{1}{2}$ $Sm_2(SO_4)_3 \cdot 8H_2O \times 10^6$	χ of Sm^{+++}
290.6	931	1038
240.2	965	1072
205.0	1001	1108
169.8	1050	1157
112.5	1168	1275
84.6	1252	1359
73.8	1295	1402

The figures in the third column were computed from the corresponding ones of the second by subtracting the diamagnetic susceptibility of $\frac{1}{2}(SO_4)_3 \cdot 8H_2O$, which was taken as -107. This susceptibility was based upon the value[11] -37 for the susceptibility of one mole $SO_4^{=}$ and -13 for one mole H_2O.

Perhaps it should be recalled that diamagnetic susceptibilities do not vary with the temperature.

It is obvious that Curie's law is not obeyed, for a four-fold change in temperature produces only about a 40% change in the susceptibility of Sm^{+++}.

The pull obtained within a few minutes at any particular temperature was the same as that observed after ten hours. Hence we may conclude that equilibrium is attained rapidly.

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[13] Cabrera, *J. phys.*, *6*, 252 (1925); St. Meyer, *Physik. Z.*, 26, 51 and 479 (1925); Zernike and James, THIS JOURNAL, 48, 2827 (1926); Decker, *Ann. physik*, 79, 324 (1926). Decker measured the ions in solution; the others measured the solid salts.

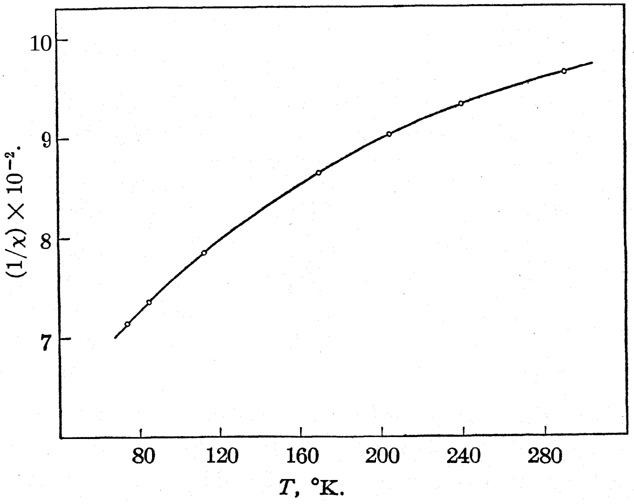
The accuracy of the relative values is probably within **0.3%.** The absolute value found for the susceptibility of Sm^{+++} at room temperature is about 4% higher than that obtained by Zernike and James and about 10% lower than that either of Cabrera or Decker.

Conclusions

It should be recalled that on the quantum theory the angular momentum j is a constant of the motion of the atomic system; that is, for a fixed energy there is a fixed angular momentum. Hence a change in j implies a change in the energy of the atom, in other words, an electronic jump. Associated with this change in j there is a change in the magnetic moment μ. In the simple case carried over from the classical theory

$$\mu = \frac{e}{2mc} j$$

The above reasoning applies also to systems of more than one electron.



Pig. 3.

Conversely, a change in the magnetic moment is accompanied by a change in j and hence by an electronic jump or rearrangement. The experimental results show that Sm^{+++} does not have a constant Curie "Constant" (C in the relation $T = C/\chi$, is not independent of the temperature). Such a variation implies that there is a mixture of several (two in the first approximation) substances of different magnetic moments whose relative amounts are varying with the temperature. In other words, there are two electronic isomers of Sm^{+++} whose relative concentrations are varying with the temperature.

The actual amounts of the two forms cannot be calculated by assuming that each form obeys Curie's law. As has been mentioned in the introduction, the existence of more than one electronic configuration immediately carries with it, according to the quantum mechanics, a term in the susceptibility which is independent of the temperature. This term may be appreciable, as Van Vleck and Frank[14] have been led to believe, from considerations based upon screening constants from x-ray data.

The fact that the effective Curie constant of Sm^{+++} decreases with diminishing temperature suggests its approach to the low value expected by Hund for the configuration

Sm^{+++}	1_1	2_1 to 4_3	4_4	5_1	5_2
	2	full	5	2	6

The existence of this isomer at the lowest temperature would bring the electronic configuration of Sm^{+++} in line with the regular sequence of the other rare earths whose magnetic moments agree with Hund's theoretical calculations. If the presence of this form is assumed, it appears that the susceptibility contains a term independent of the temperature also. (The existence of such a term could be more readily decided by a determination of the susceptibility at the temperature of liquid hydrogen, which it is hoped to make soon.)[15]

A striking confirmation of the existence of a mixture of electronic isomers was obtained in collaboration with Dr. Frank H. Spedding,[16] from the absorption spectra of a crystal of trivalent samarium taken at different temperatures, from that of liquid hydrogen to room temperature. Certain lines in the spectrum of Sm^{+++} prominent at room temperature became faint at the temperature of liquid air and practically disappeared at that of liquid hydrogen. On the other hand, lines which were intense at the temperature of liquid hydrogen became much fainter at room temperature. This variation in relative intensity reveals the presence of different electronic isomers whose relative concentration is varying with the temperature. The isomer stable at the lowest temperature becomes more plentiful at lower temperatures and its increased concentration manifests itself in the increased intensity of the light it absorbs.

The magnetic susceptibility of Sm^{+++} in solution[17] is practically identi-

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[14] Van Vleck and Frank, *Phys. Rev.,* 34,1494,1625 (1929).

[15] The experimental values do not agree with assumptions of Van Vleck and Frank that $\Delta\nu$ between the configurations of different values of j can be calculated from the Goudsmit generalization of the Sommerfeld relativity formula. The latter leads to a $\Delta\nu$ of 940 cm.$^{-1}$ between the two lowest energy levels and the corresponding Boltzmann factor shows that only 1% of Sm^{+++} is electronically activated at room temperature (with a contribution to susceptibility of about 4%) and even less, of course, at lower temperatures. Hence the difference between the measured susceptibility and the part obeying Curie's law should give values which are practically the same for all temperatures. Such is not the case.

[16] Freed and Spedding, *Nature,* 123, 525 (1929). The magnetic results on Sm^{+++} were first referred to here.

[17] Decker, *Ann. Physik,* 79, 324 (1926), see Table I.

cal with that in the crystal. Hence the electronic isomers are present in solution to the same concentration as in the crystal at the same temperature.

Summary

The magnetic susceptibility of $Sm_2(SO_4)_3 \cdot 8H_2O$ was measured from 73.8 to 290.6°K. by a new accurate method.

It was found that Sm^{+++} both in the solid state and in solution consists of a mixture of electronic isomers. These isomers appear to be in thermal equilibrium.

The variation of the susceptibility with the temperature suggests that the isomer stable at the lowest temperature has the electronic configuration

Sm^{+++}	1_1	2_1 to 4_3	4_4	5_1	5_2 electronic shell
	2	full	5	2	6 number of electrons

but such *a* configuration is not yet completely established.

The conclusion that Sm^{+++} consists of a mixture of electronic isomers varying in concentration with the temperature carried with it the prediction that its absorption spectrum would consist of lines whose relative intensities would vary with the temperature. Such a variation in the intensities of the lines was actually found (in collaboration with Dr. F. H. Spedding)[16] in the absorption spectrum of $SmCl_3 \cdot 6H_2O$ taken from room temperature to that of liquid hydrogen.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COOPERATION WITH THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITIES AT LOW TEMPERATURES OF ANTIMONY, ANTIMONY TRIOXIDE, ANTIMONY TETROXIDE AND ANTIMONY PENTOXIDE[1]

BY C. TRAVIS ANDERSON[2]

RECEIVED MARCH 26, 1930 PUBLISHED JULY 3, 1930

In a previous paper from the Pacific Experiment Station of the United States Bureau of Mines the author presented low-temperature thermal data for arsenic and its oxides. The present paper deals with the heat capacities of antimony and its oxides. The third and last of this group on bismuth and its oxides will appear later.

The method and apparatus have been described previously.[3]

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Assistant Physical Chemist, Pacific Experiment Station, U. S. Bureau of Mines, Berkeley, California.

[3] Anderson, THIS JOURNAL, 52, 2296 (1930).

Materials

The sample of antimony used was analyzed for arsenic, lead and insoluble matter, and contained less than 0.2% total of these materials. It was therefore of sufficiently high purity. It had a density of 6.74 at 24.1°; 388.5 g. was used for the determinations. The antimony trioxide was material of C. P. grade, which was resublimed, yielding orthorhombic crystals. Each particle was definitely crystalline. The portion used was exceptionally pure, analyzing better than 99.9% Sb_2O_3. Its density was found to be 5.99 at 27.4°. The calorimeter was filled with a 284.0-g. sample.

The antimony tetroxide was made by boiling a mixture of the antimony oxides with concentrated nitric acid for some time. The sample was washed free from nitric acid, dried, and heated in a silica flask, which was continuously evacuated at 850°. The resulting product was analyzed for tri- and pentavalent antimony and had the correct ratio for Sb_2O_4. It had a density of 6.47 at 23.8°. A 236.6-gram sample was studied.

Two samples of antimony pentoxide were used. They were prepared by the hydrolysis of antimony pentachloride. About 1 kg. of antimony pentachloride was twice distilled in an atmosphere of chlorine and once in *vacuo.* The resulting pure antimony pentachloride was then poured, very slowly, into a very large volume of cold water. The hydrolyzed precipitate of antimonic oxychloride was allowed to settle and washed by decantation ten to fifteen times. The precipitate was then dialyzed for several months until chlorides were undetectable, and finally filtered and dried. According to Simon and Thaler[4] it is impossible to prepare pure dry antimony pentoxide in this manner. The air-dried material contains between 4.4 and 4.6 formula weights of water per formula weight of antimony pentoxide. Therefore, the sample of hydrated oxide obtained was divided into two parts. One part was heated in a silica flask and was evacuated continuously for three days at 360°. The analysis of the resulting material was as follows: water, 1.5%; Sb_2O_3, 6.45%; Sb_2O_5, 92.05%. Assuming that the Sb_2O_3 is combined with the Sb_2O_5 to form Sb_2O_4, we have Sb_2O_4, 13.6% and Sb_2O_5 84.9%. This gives a sample of Sb_2O_5 containing 0.317 formula weight of water per formula weight of Sb_2O_5, which corresponds very well with the analysis of Simon and Thaler for their oxide, which had been heated at this temperature. In calculating the specific heats a correction was made for the 13.6% of Sb_2O_4 which was present in this sample. The density of the $Sb_2O_5 \cdot 0.317\,H_2O$ was 5.14 at 24.8°; 100.8 g. of the material was used for making the measurements.

The other portion of hydrated antimony pentoxide was dried in air at 130° for several days. No detectable decomposition of the antimony pentoxide takes place at this temperature. The resulting sample analyzed 11.02% of H_2O and 88.98% of Sb_2O_5, which gives 2.224 formula weights of water per formula weight of antimony pentoxide. These values are also in excellent agreement with those of Simon and Thaler. The

TABLE I

SCREEN SIZES (TYLER) OF SAMPLES

Screen size	Sb, %	Sb_2O_3, %	Sb_2O_4, %
+ 35	..	27.0	..
+ 48	3.5	7.0	..
+ 65	24.0	8.5	..
+100	20.0	9.5	3.0
+150	10.0	5.5	16.0
+200	15.5	10.5	38.0
−200	27.0	32.0	43.0

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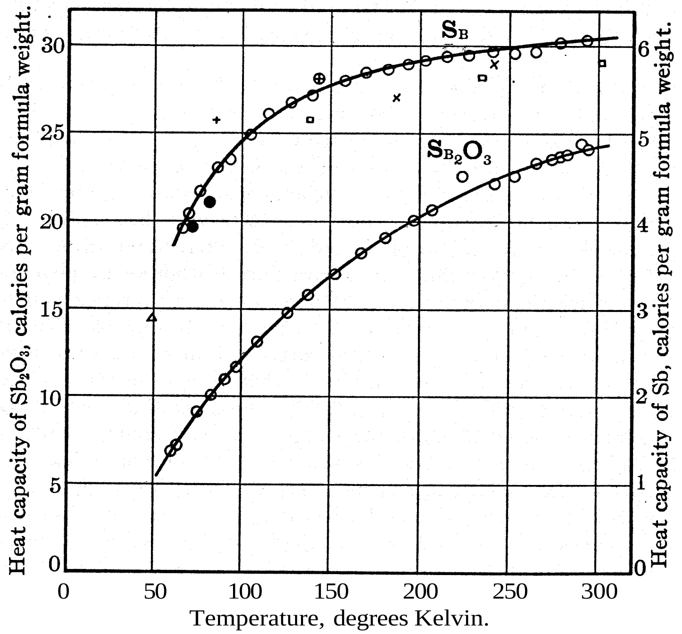
[4] Simon and Thaler, *Z. anorg. allgem. Chem.,* 162, 113, 253 (1927).

density of this sample of oxide was 4.32 at 26.2°. The calorimeter was filled with 138.7 g. of the material.

Screen tests using Tyler screens were made on these materials, except the antimony pentoxide, which was extremely finely divided. The results are shown in Table I.

The Specific Heats

No previous measurements have been made at low temperatures on any of the oxides of antimony. Several determinations, however, have been made on antimony metal.[5]



○, Anderson; □, Ewald; ●, Simon and Ruhemann; ⊕, Richards and Jackson; X, Schimpff; +, Giinther; A, Dewar.

Fig. I.--The heat capacity of antimony and antimony trioxide in calories per gram formula weight.

With the exception of those of Giinther and of Simon and Ruhemann, the determinations were mean specific heats. Of the true specific heats, Giinther and Simon and Ruhemann have several determinations, but over a very small temperature range. While their determinations are within a few degrees of one another, the values they have obtained are far from being in agreement.

[5] Richards and Jackson, *Z. physik. Chem.*, ***70***, 414 (1910); Schimpff, *ibid.*, 71, 257 (1910); Dewar, ***Proc. Roy. Soc.*** (London), **A89,** 158 (1913); Ewald, ***Ann. Physik,*** 44, 1213 (1914); Giinther, *ibid.*, [4] 63, 476 (1920); Simon and Ruhemann, ***Z. physik. Chem.,*** 129, 321 (1927).

The results obtained in this research for the pure substances are shown graphically in Figs. 1 and 2. The various values obtained by other investigators on the heat capacity of antimony are also shown for comparison.

The experimental determinations of heat capacities for antimony, antimony trioxide, antimony tetroxide and the two samples of antimony pentoxide expressed in g. calories (15°) per gram formula weight are given in Table II. The $Sb_2O_5 \cdot 0.317\ H_2O$ has been corrected for the Sb_2O_4 present in the sample. In changing joules to calories the factor[6] 1/4.184 was used. The calculations were made on the basis of Sb = 121.77 and O = 16.

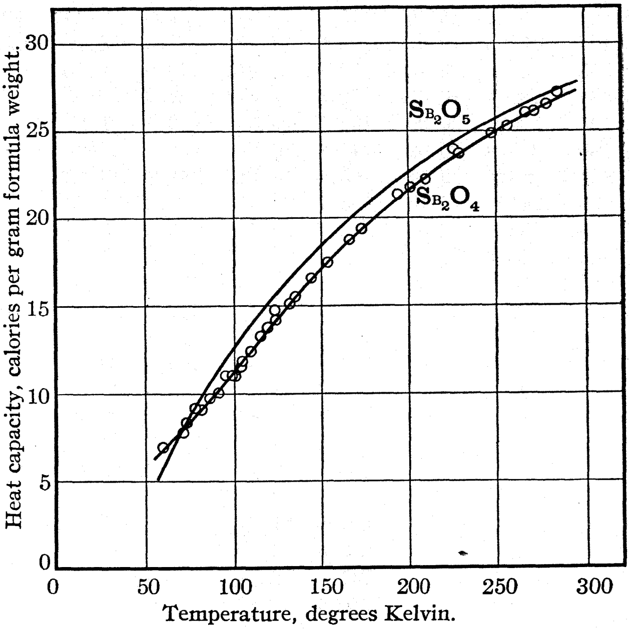


Fig. 2.—The heat capacities of antimony tetroxide and antimony pentoxide per gram formula weight.

The temperature scale is probably accurate within ±0.1°. On the average the heat capacity measurements at 55°K. have an error of about 1%. This is due largely to the diminishing resistance and the decrease of temperature coefficient of the copper resistance thermometer. As the temperature increases above 55° the error decreases to about 0.5% at 100°K. From this temperature the error slowly increases to about 1% at 300°K.

The results for the anhydrous antimony pentoxide were obtained from measurements of two hydrated samples. The uncertainty of composition may be greater than the error of measurement, exclusive of the fact that two series of measurements are involved.

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[6] "International Critical Tables," Vol. I, p. 24. 4.185 abs. joules = 1 cal. = 4.1837 Int. joules.

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT

Sb		Sb_2O_3		Sb_2O_4		$Sb_2O_5\cdot0.317$ Hz0		$Sb_2O_5\cdot2.224\ H_2O$	
T, °K.	C_p	T, °K.	C_p	T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
...	...	59.8	6.893	72.8	8.317	63.6	7.283	60.6	10.46
66 0	3.917	63.2	7.189	77.3	9.157	68.0	8.138	64.8	11.60
69.6	4.083	74.7	9.114	80.1	9.061	72.9	9.125	86.7	16.94
75.7	4.337	82.6	10.06	85.6	9.723	77.8	10.01	101.9	20.45
85 8	4.602	90.6	10.97	90.6	10.02	82.1	10.83	125.6	26.16
93.1	4.700	97.2	11.64	94.4	11.02	89.5	11.36	150.3	30 86
104.6	4 982	108.7	13.11	98.5	11.00	101.5	13.31	184.1	36.94
114.8	5.224	125.9	14.79	104.3	11.83	112.7	15.55	209.9	41.41
127.7	5.351	137.4	15.76	115.7	13.64	127.6	17.49	248.1	46.23
139.7	5.431	152.3	16.97	122.6	14.72	133.3	18.19	272.5	49.28
157.9	5.598	167.0	18.18	59.8	6.942	142.9	19.25	280.5	51 07
169.4	5.691	180.4	19.05	70.8	7.756	153.9	20.57	292.1	52.27
181 9	5.726	196 6	20.06	134.5	15.50	162.4	21.57		
193.0	5.789	206.8	20.69	143.8	16.57	171.1	22.69		
2026	5834	223.7	2254	165.6	18.74	181.7	23.42		
214.5	5.878	241.8	22.15	193.7	21.37	197.2	24.70		
227.0	5.893	252.9	22.59	209.7	22.20	201.8	25.05		
240.6	5.943	265.2	23.32	226.1	23.94	210 3	25.21		
252.9	5.923	274.6	23.57	1001	11.00	221.8	27.05		
2645	5.940	278.9	23.72	103.7	11.51	233.1	27.89		
278.4	6.043	282.8	23.83	109.0	12.41	241.3	28.02		
293.2	6.073	290.5	24.49	114.8	13.25	256.3	28.96		
		2944	24.11	118.8	13.75	269.6	2962		
				123.1	14.17	282.1	28.42		
				131.3	14.11	289.7	31.29		
				153.1	17.44	287.8	30.53		
				172.7	19.37				
				200.9	21.74				
				229.3	23.70				
				247.8	28.84				
				256.4	25.23				
				266.9	26.01				
				271.9	26.10				
				278.8	26.50				
				284.9	27.17				

In Table III are shown in Columns (a) and (b) the values for the heat capacities per gram formula weight of $Sb_2O_5\cdot2.224\ H_2O$ and $Sb_2O_5\cdot0.317\ H_2O$, respectively, which were read at even values of the temperatures from smooth curves representing the experimental data. In (c) the differences between these heat capacities are tabulated, representing 1.907 formula weights of water, corresponding to the difference in the composition of these two oxides. The values in Column (d) represent the heat capacities per formula weight of anhydrous antimony pentoxide, which were calculated as follows.

$$C_p(Sb_2O_5) = C_p(Sb_2O_5\cdot0.317\ H_2O) - \frac{0.317}{1.907}\left[C_p(Sb_2O_5\cdot2.224\ H_2O) - C_p(Sb_2O_5\cdot0.317\ H_2O)\right]$$

This obviously assumes that the heat capacity per formula weight of the water present in these two samples is independent of the amount, up to 2.224 formula weights of water per formula weight of antimony pentoxide. In (e) are shown the heat capacities per formula weight of this combined water, which are compared graphically in Fig. 3 with the known heat capacity of ice as given by Simon.[7] Values in Columns (a) and (b) are also shown on this graph.

TABLE III

THERMAL DATA ON ANTIMONY PENTOXIDE

T, °K.	(a) $C_p Sb_2O_5 \cdot 2.224\ H_2O$	(b) $C_p Sb_2O_5 \cdot 0.317\ H_2O$	(c) Difference	(d) $C_p(Sb_2O_5)$	(e) $C_p(H_2O)$
60	10.30	6.48	3.82	5.75	2.00
70	12.83	8.54	4.29	7.83	2.25
80	15.33	10.47	4.86	9.66	2.55
90	17.78	12.21	5.57	11.28	2.92
100	20.14	13.73	6.41	12.66	3.36
110	22.42	15.20	7.22	14.00	3.79
120	24.61	16.52	8.09	15.17	4.24
130	26.76	17.78	8.98	16.29	4.71
140	28.85	19.02	9.83	17.39	5.15
150	30.79	20.22	10.57	18.46	5.54
160	32.67	21.32	11.35	19.43	5.95
170	34.50	21.34	12.16	20.32	6.38
180	36.26	23.33	12.93	21.18	6.78
190	38.02	24.24	13.78	21.95	7.23
200	39.71	25.10	14.61	22.67	7.66
210	41.28	25.89	15.39	23.33	8.07
220	42.77	26.67	16.10	23.99	8.44
230	44.13	27.38	16.75	24.59	8.78
240	45.43	27.99	17.44	25.09	9.15
250	46.74	28.58	18.16	25.56	9.52
260	48.05	29.17	18.88	26.03	9.90
270	49.38	29.80	19.58	26.54	10.27
280	50.70	30.44	20.26	27.07	10.62
290	52.03	31.10	20.03	27.62	10.98
300				(28.23)	

Calculation of Entropies

The conventional method was used in calculating the entropies. The experimental heat capacity curves were extended below the lowest measure-

TABLE IV

ENTROPIES FROM EXPERIMENTAL DATA

	Sb	Sb_2O_3	Sb_2O_4	Sb_2O_5
Extrap. (0–56.2)°K.	1.91	4.09	4.31	2.54
Graph (56.2–298.1)	8.59	25.35	26.04	27.32
$S°_{298}$	10.5 ± 0.2 E. U.	29.4 ± 0.4 E. U.	30.3 ± 0.5 E. U.	29.9 ± 1 E. U.

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[7] Simon, "Handbuch der Physik," Verlag Julius Springer, Berlin, **1926,** Vol. X, p. 360.

ments to approach and finally coincide with Debye functions having the following parameters (Θ): for Sb, 201; Sb_2O_3, 126; Sb_2O_4, 121 and Sb_2O_5, 183. In Table IV are given the results of the entropy calculations.

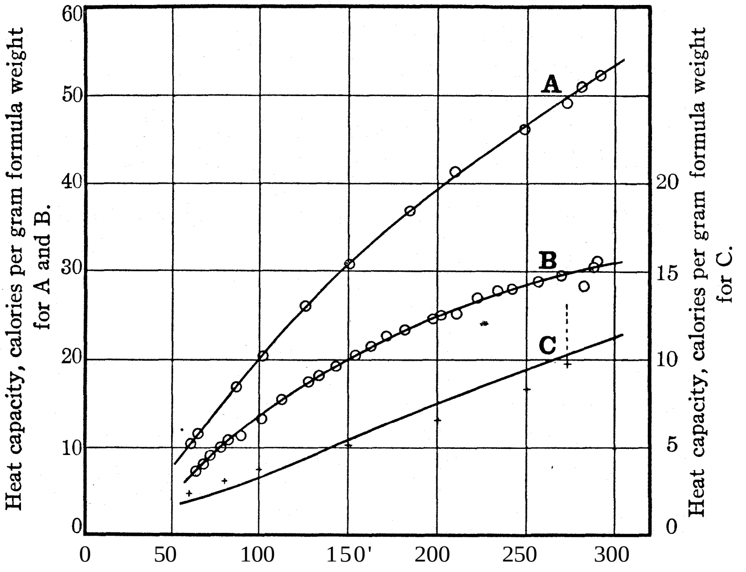

Fig. 3.—Curve A, $Sb_2O_5 \cdot 2.224\ H_2O$; Curve B, $Sb_2O_5 \cdot 0.317\ H_2O$; Curve C, combined H_2O; +, values for H_2O given by Simon in "Handbuch der Physik."

The following combinations of Debye and Einstein functions were found to fit the specific heat curves per formula weights for the three oxides

$$C_{Sb_2O_3} = D\frac{(126)}{T} + 2E\frac{(557)}{T} + 2D\frac{(542)}{T}$$

$$C_{Sb_2O_4} = D\frac{(121)}{T} + 2E\frac{(314)}{T} + 3E\frac{(757)}{T}$$

$$C_{Sb_2O_5} = D\frac{(183)}{T} + 2E\frac{(303)}{T} + 2E\frac{(532)}{T} + 2E\frac{(1504)}{T}$$

The Sb_2O_3 combination fits the experimental results up to 298°K., the Sb_2O_4 combination to above 260°K., and that for Sb_2O_5 to about 160°K. Above 260°K. for Sb_2O_4 and 160°K. for Sb_2O_5 the experimental curves rise above those of the function sums, which is due in part to the increase in $C_p - C_v$.

To demonstrate the average agreement between the experimental data and these combinations the entropies of the oxides at 298°K. were calculated by use of these function sums. The results obtained are: for Sb_2O_3, 28.9 E. U.; for Sb_2O_4, 29.6 E. U.; and for Sb_2O_5, 30.4 E. U. It was necessary to add 0.03 unit to the result obtained by the Sb_2O_4 combinations and

0.32 unit to the value obtained by the Sb_2O_5 functions for the rise in C_p above the values given by the function sums. These results agree very well with the experimental values given in Table IV.

A comparison of the general trend of the specific heat curves, the entropies at 298°K., and the theoretical functions which have been used to fit the data empirically indicates (but, of course, does not prove) that the crystalline oxides of antimony have similar structures.

Related Thermal Data

The heats of formation of the three oxides have been determined by Mixter[8] by the combination of antimony and its oxides with sodium peroxide. Biltz[9] has calculated the heat of formation from decomposition pressure measurements by the use of Nernst's approximation formula. Simon and Thaler[10] from their decomposition pressure measurements have similarly calculated the heats of formation. The various values, however, are in very poor agreement. Owing to Mixter's method of preparation of antimony pentoxide, there is considerable doubt as to the purity of his material, and consequently no reliance can be placed on his results, as they are all based on thermal measurements on his antimony pentoxide. It is also a well-known fact that the Nernst approximation formula often leads to the calculation of very erroneous thermal data. Consequently no attempt will be made to utilize any of these values in the calculation of free energies.

Schuhmann[11] and Roberts and Fenwick[12] have calculated the free energy of Sb_2O_3 from all measurements. Schuhmann gives ΔF°_{298} for $Sb_2O_3 =$ $-148{,}600$ Cal. While he does not so state, he probably worked with the orthorhombic form or a mixture. Roberts and Fenwick give $-149{,}690$ Cal. for the cubic. For the change Sb_2O_3 (orthorhombic) = Sb_2O_3 (cubic), the latter gives $\Delta F^\circ_{298} = -1800$ Cal., so that the free energy of the orthorhombic form would be $-147{,}900$ Cal. Since the orthorhombic form was used in the present work, the value $-147{,}900$ Cal. may be used in combination with the measured entropies of Sb and Sb_2O_3 and the accepted entropy of O_2 to calculate the heat of formation of Sb_2O_3 as $\Delta H^\circ_{298} = -167{,}300$ Cal. This value is in rather poor agreement with the value of $-165{,}000$ Cal. obtained by Mixter. This value has been corrected for the newer value for the atomic weight of antimony.

In conclusion the author wishes to thank R. W. Millar for making the measurements on antimony trioxide, C. G. Maier for his many helpful suggestions and material assistance, and K. K. Kelley for his assistance in

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[8] Mixter, *Am. J. Sci.*, [4] 28, 103 (1909).

[9] Biltz, *Nach. kgl. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 293 (1908).

[10] Simon and Thaler, *Z. anorg. allgem. Chem.*, 162, 253 (1927).

[11] Schuhmann, THIS JOURNAL, 46, 52 (1924).

[12] Roberts and Fenwick, *ibid.*, 50, 2125 (1928).

calibrating thermocouples, making a new temperature scale, and in checking the numerous calculations necessary in the determination of the entropies.

Summary

The heat capacities of antimony, antimony trioxide, antimony tetroxide and antimony pentoxide, from about 60 to 300°K., have been determined and their corresponding entropies calculated. The heat of formation of antimony trioxide has been calculated.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COOPERATION WITH THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITIES OF BISMUTH AND BISMUTH TRIOXIDE AT LOW TEMPERATURES[1]

BY C. TRAVIS ANDERSON[2]

RECEIVED MARCH 27, 1930 PUBLISHED JULY 3, 1930

This is the third of a series of papers from the Pacific Experiment Station of the United States Bureau of Mines dealing with thermal data of the metals and oxides of the fifth group of the periodic system. Two previous articles[3] have dealt with the metals arsenic and antimony and their oxides. This paper presents the results for bismuth metal and bismuth trioxide.

Materials

The bismuth metal used was a sample of high purity kindly furnished by the American Smelting and Refining Company. No detectable amounts of lead, arsenic, or antimony were found on analysis. It had a density of 9.86 at 20.6". The calorimeter was filled with a 552-g. sample of granular metal.

TABLE I

SCREEN SIZES (TYLER) OF BISMUTH AND BISMUTH TRIOXIDE

Screen sizes	Bi, %	Bi_2O_3, %
+ 35	..	1.5
+ 48	..	12.5
+ 65	17.0	12.0
+100	29.5	13.5
+150	14.5	8.5
+200	17.5	16.5
−200	21.5	35.5

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

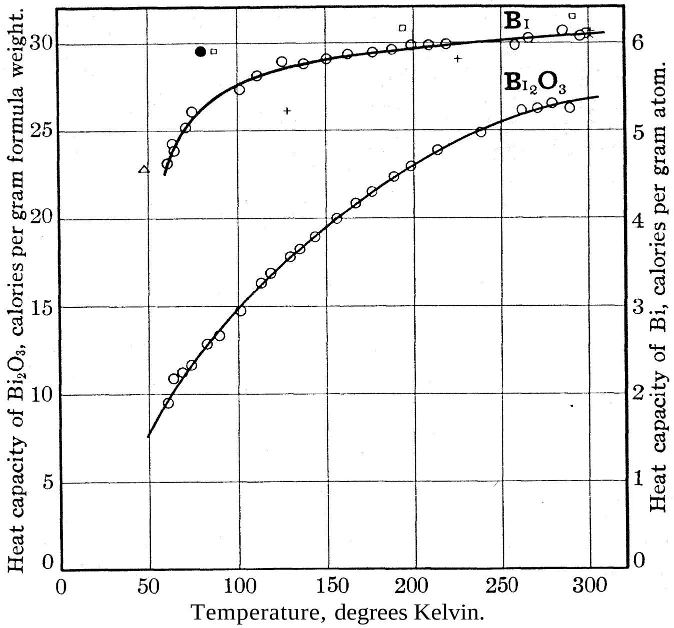
[2] Assistant Physical Chemist, Pacific Experiment Station, U. S. Bureau of Mines, Berkeley, California.

[3] Anderson, THIS JOURNAL, 52,2296, 2712 (1930).

The sample of bismuth trioxide was of C. P. grade. On reduction with hydrogen it was found to consist of 99.6% Bi_2O_3 and was of sufficiently high purity. Its density was found to be 9.33 at 23.3°. A 356-g. sample was used for the determinations.

Screen tests, using Tyler screens, were made on the bismuth and bismuth trioxide, and the results are shown in Table I.

The Specific Heats.—-No measurements have been made on bismuth trioxide at low temperatures. Several determinations, however, have been made on bismuth metal.[4]



○, Anderson; ×, Jaeger and Diesselhorst; +, Ewald; □, Giebe; A, Dewar; ●, Richards and Jackson.

Fig. 1.—The heat capacities of bismuth and bismuth trioxide in calories per gram formula weight.

All of the determinations are mean specific heats. The various values obtained by these investigators on the heat capacity of bismuth are shown in Fig. 1. The results obtained in this Laboratory on the heat capacity of bismuth and bismuth trioxide, expressed in gram calories (15°) per gram formula weight, are given in Table II and are also shown graphically in

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[4] Jaeger and Diesselhorst, *Wiss. abh. Phys.-Tek. Reich,* **3,** *269* (1900); Giebe, *Verhandl. deut. physik. Ges.,* *5,* 60 (1903); Richards and Jackson, *Z. physik. Cham.,* **70,** *414* (1910); Schimpff, *ibid.,* 71, 257 (1910); Dewar, *Proc. Roy. Soc.* (London), **A89,** 158 (1913); Ewald, *Ann. Physik,* 44, 1213 (1914).

Fig. 1. In changing joules to calories the factor[5] 1/4.184 was used. The calculations were made on the basis of Bi = 209.0 and O = 16.

The accuracy of the measurements has been discussed previously[6] and will apply to both bismuth and bismuth trioxide.

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT

Bi		Bi		Bi_2O_3		Bi_2O_3	
T, °K.	C_p	T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
60.8	4.631	176.8	5.899	289.3	26.25	118.6	16.86
64.7	4.771	187.7	5.924	262.1	26.17	129.2	17.80
63.4	4.851	198.9	5.976	271.4	26.29	143.1	18.93
71.1	5.040	208.8	5.974	279.7	26.54	155.7	19.96
74.6	5.216	218.8	5.980	60.6	9.50	166.4	20.85
101.3	5.464	258.1	5.874	63.7	10.89	175.8	21.49
111.2	5.674	266.3	6.058	68.7	11.24	188.5	22.35
125.1	5.813	272.8	6.083	73.6	11.64	198.2	22.95
137.2	5.761	285.3	6.139	82.6	12.85	134.7	18.24
150.2	5.817	295.2	6.089	89.3	13.32	213.3	23.87
162.5	5.869	298.2	6.104	101.4	14.72	238.4	24.88
				113.0	16.31		

Calculation of Entropies.—The entropies were determined by the usual graphical method. The experimental heat capacity curves were extrapolated from the lower points so as to coincide with Debye functions having the parameters (Θ) for Bi 147, and for Bi_2O_3, 97. In Table III are given the results of the entropy calculations.

TABLE III

ENTROPIES FROM EXPERIMENTAL DATA

	Bi	Bi_2O_3
Extrap. (0–56 2)°K.	3.13	6 22
Graph (56.2–298.1)	9.31	29 96
S°_{298}	12.4 ± 0.3 E. U.	36.2 ± 0.4 E. U.

The following combination of Debye and Einstein functions was found to fit the experimental specific heat curve per gram formula weight of Bi_2O_3 up to 178°K.

$$C_{Bi_2O_3} = D\left(\frac{97}{T}\right) + 2E\left(\frac{225}{T}\right) + 2E\left(\frac{568}{T}\right)$$

Above 178°K. the experimental curve rises above that of the function sum.

The entropy of Bi_2O_3 by use of this function sum was calculated to be 36.4 E. U. It was necessary to add 0.24 unit to the results obtained by the combinations for the rise in C_p above the value given by the function sum.

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[5] "International Critical Tables," Vol. I, p. 24. 4.185 abs. joules = 1 cal. = 4.1837 Int. joules.

[6] Anderson, THIS JOURNAL, 52, 2712 (1930).

It was not found possible to prepare samples of Bi_2O_4 or Bi_2O_5 of sufficient purity to determine their specific heats. However, by comparison of the entropies of arsenic and antimony it is suggested that until the entropies are actually determined, the value 35.0 ± 2 E. U. may be used for each, with reasonable assurance.

Related Thermal Data.—The heat of formation of Bi_2O_3 has been determined by Mixter[7] and Ditte and Metzner.[8] Mixter gives $-136,000$ cal., and Ditte and Metzner gives $-137,800$ cal.

Using Mixter's values of $-136,000$ cal. with the measured entropies of Bi and Bi_2O_3 and the accepted entropy of O_2, the free energy of Bi_2O_3 is calculated as $-118,000$ cal.

In conclusion the author wishes to thank K. K. Kelley for his assistance in making the new temperature scale and in checking the calculations in the determinations of the entropies.

Summary

The heat capacities of bismuth and bismuth trioxide from about 60 to 300°K. have been determined and their corresponding entropies calculated. The free energy of Bi_2O_3 has been calculated.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

THE SURFACE TENSION OF LIQUID NITROUS OXIDE

BY ELTON L. QUINN AND GRANT WERNIMONT

RECEIVED MARCH 31, 1930 PUBLISHED JULY 3, 1930

Many investigators find carbon dioxide and nitrous oxide an interesting pair of compounds largely because of the similarity of their physical properties. The close agreement between the densities, vapor pressures, critical temperatures, molecular weights, etc., is very remarkable, and it is not uncommon to group them together when considering questions pertaining to their physical make-up. The fact that such an agreement does not extend to the chemical behavior of these two substances, enhances this interest as it indicates that the physical properties are related more to the arrangement of the atoms in the molecules than to the ultimate constitution of the atoms.

Niven[1] gives reasons quite sufficient for concluding that carbon dioxide and nitrous oxide have the same electronic arrangement. Rankine[2] shows from crystal structure data and viscosity data, the similarity in structure of molecules of the two compounds. Many other investigators have dealt

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[7] Mixter, *Am. J. Sci*, [4] 28, 103 (1909).

[8] Ditte and Metzner, *Compt. rend.*, 115, 1303 (1892).

[1] Niven, *Phil. Mag.*, [7] 3, 1314–1334 (1927).

[2] Rankine, *Proc. Roy. Soc.* (London), **A98**, 369–374 (1921).

with this problem in various ways, and in all cases their results indicate a remarkable similarity in the structure of the two kinds of molecules.

It seemed to the authors that any data on the forces acting between the molecules of carbon dioxide and nitrous oxide might be of interest, not only as affecting these compounds, but also from the general point of view of surface tension and solubility. This paper will be devoted to the study of the surface tension of liquid nitrous oxide, from which an attempt to estimate its internal pressure will be made, while a later publication will deal with the internal pressure from a determination of the solubility of various solutes in liquid nitrous oxide. Carbon dioxide has already been studied from this point of view.

The surface tension of liquid nitrous oxide was first determined by Verschaffelt[3] over a temperature range from 25 to −25°, and later by Grunmach,[4] who made four determinations over a temperature range from 20 to −90°. Verschaffelt used the capillary tube method while Grunmach used the so-called capillary wave method. The original paper of Verschaffelt was not available to the authors, so it was not possible to determine just what was done about the density of the saturated vapor over the liquid nitrous oxide. As far as the authors are aware, no reliable determinations of the densities of the gaseous and liquid phases of nitrous oxide below 0° have ever been made previous to those recently published.[5]

Preparation of Tubes

The capillary tubes used in these measurements were drawn from soft "soda glass" tubing. Before drawing, the larger tubes were carefully cleaned and dried. A large number of such tubes were made and pieces from these were carefully selected in order to insure a circular cross section and a uniform bore. The ends of these capillaries were measured with a microscope and the variation in the length of a thread of mercury, moved along the tube, was used to indicate uniformity of bore. The exact diameter of each tube selected was determined, at a point to which it was estimated the liquid would reach, during the capillary measurements, by the usual method of weighing a thread of mercury of known length. These measurements were checked after the measurements of capillary rise by cutting the capillaries at the average height reached by the liquid, and measuring the internal diameter of the cut ends with a microscope. The agreement between the results of these two methods of measurement was quite satisfactory. Before the capillary tubes were placed in the jackets in which the liquid nitrous oxide was to be condensed, they were boiled with a cleaning solution of chromic acid, washed many times with distilled water and finally dried in a current of dry, dust-free air. Each capillary was supported in the center of a larger outer jacket by means of platinum wires. The outside tubes were very carefully made from thick-walled pyrex glass tubing having an internal diameter of about 16 mm. and a wall thickness of 3 mm. It was desirable to have the diameter of these tubes large in order to keep any correction occasioned by them as low as possible. These tubes proved to be very satisfactory and none of them failed during the period of this investigation.

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[3] Verschaffelt, Comm. Phys. Lab. Univ. Leiden, No. 18, 640 (1895).

[4] Grunmach, *Ann. Physik,* [4] 15,401 (1904).

[5] Quinn and Wernimont, THIS JOURNAL, 51,2002 (1929).

The nitrous oxide was obtained from a commercial cylinder of the liquid manufactured by the Ohio Chemical Company. A very careful qualitative analysis showed that it was free from other oxides of nitrogen. halogens, carbon dioxide, sulfur compounds arid ammonia. In some preliminary tests the gas was distilled into the pyrex tubes from the liquid through a calcium chloride tower 55 cm. long. When the temperature of this liquid was lowered to about 10 or 20° below zero, a few very fine crystals separated. It was assumed that this impurity was water so a glass trap filled with short pieces of aluminum wire was placed in the line. Into this trap the nitrous oxide was distilled after passing through the calcium chloride. It was condensed to a liquid, at a temperature close to the freezing point of the nitrous oxide, and vaporized again at a temperature of about —50". This vapor was conducted to the pyrex tube containing the capillary and again condensed to a liquid, then frozen to a solid and while in this state the tube was sealed. After this treatment, no solids ever separated at any temperature from the liquid nitrous oxide and this was considered evidence that the water had been successfully removed. The distillation method of purification, which has already been described,[5] is considered by the authors to be superior to this, but the work on surface tension had already been completed before this distillation process was developed. There are many reasons for believing, however, that the liquid nitrous oxide used in this investigation was very pure.

To facilitate the handling of the pyrex tube containing the liquid nitrous oxide, it was placed in a larger tube sealed at one end and about 65 cm. (2 feet) long. A ring of paper at the top and a wad of cotton on the bottom held this tube firmly in position.

The thermostat used and the method of measuring the capillary rise has already been described by one of us[6] and this procedure was modified only slightly in the present investigation.

Calculations

Calculation of surface tension from the liquid rise in a capillary tube placed in the center of a larger tube makes several corrections necessary and some of these are difficult to evaluate. The effect of the weight of the liquid in the small meniscus above the point of measurement has been pretty well worked out and in a small tube of capillary size the measured height is usually corrected by the addition of $r/3$, where r is the radius of the capillary. The effect of the outer jacket on the rise of the liquid in the capillary tube is somewhat more difficult to determine. This question has received considerable attention from Richards and his co-workers at Harvard University but the apparatus used by these workers could not be adapted easily to this investigation because of the high pressures used. The method and apparatus used by Sugden[7] could have been employed but certain difficulties, especially those of obtaining accurate readings of the very small capillary rise near the critical temperature, made it seem unwise. It was believed, however, that Sugden's method of calculation could be used to calculate the effect of the outer jacket on the capillary rise, especially as it seemed very likely that any such effect would be much below the experimental error. It was found that the meniscus of the liquid in the outer jacket was sufficiently flat even at the lowest temperatures to be read easily

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[6] Quinn, THIS JOURNAL, **49,** 2704 (1927).

[7] Sugden, J. Chem. *Soc.*, **119, 1483** (1921).

and that the capillary tube, standing in the center, caused no serious distortion of the surface.

It should be noted that Sugden's method of calculating the effect of the larger tube on the capillary rise in the smaller one is based on two tubes standing parallel to each other and connected at the bottom. The system used in this work is somewhat different and the capillary tube itself is bound to have some effect on the action of the larger tube, but, as will be shown later, this effect must be so small that it need not be considered here. Verschaffelt[8] has worked out a graphical method of treating a system such as was used in this work but as his original paper was not available to the authors, no attempt was made to use it.

Table I gives the values for the capillary constant a^2 in mm.^{2} for tube No. 7 at nine temperatures. The first values of a^2 were calculated from the equation $a^2 = r(h_0 + r/3)$, in which r is the radius of the capillary, h_0 is the measured height in mm. above the meniscus in the outer jacket and $r/3$ is the correction for the liquid in the small meniscus in the capillary tube. In this calculation the effect of the outer jacket on the height of the liquid in the capillary is not taken into consideration. In the third column the values for a^2 are calculated by means of Sugden's method, which takes this effect into consideration. It will be noted that the agreement between the two sets of values is quite remarkable and indicates that no correction is necessary when dealing with tubes of the sizes used in this investigation, and when using liquids with such low surface tensions. As there might be some question about neglecting the effect of the capillary tube in reducing the effective diameter of the larger tube, one calculation was made on the same tube at the lowest temperature, where any such effect would be greatest, and the absurd assumption was made that the capillary decreased the effective diameter of the tube by one-half. This calculation gave a value for a^2 which was only 1% above that actually obtained.

TABLE I

SHOWING THE EFFECT OF THE OUTER JACKET ON THE CAPILLARY RISE

Measurements on Tube No. 7 were used for these calculations

Temp., °C.	$a^2 = r(h_0 + r/3)$	a^2 (Sugden's method)	Difference, %
30	0.2443	0.2437	−0.20
20	0.6495	0.6490	− .10
10	1.0123	1.0126	+ .03
0	1.334	1.335	+ .10
−10	1.635	1.635	.00
−20	1.983	1.983	.00
−30	2.255	2.256	+ .05
−40	2.508	2.508	.00
−50	2.847	2.848	+ .03

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[8] Verschaffelt, Bull. *acad.* roy. *méd.* ***Belg.*** Cl. *Sci.*, 574 (1921).

In Table II the values of a^2 were calculated from $r(h_0 + r/3)$ for each reading. The average of these values at each temperature was taken and the surface tension γ was calculated from the equation $y = 0.5a^2g(D - d)$ in which g is the acceleration due to gravity, D is the density of the liquid

Table II

Surface Tension Measurements of Liquid Nitrous Oxide

Temp., °C.	Tube no.	h_0, cm.	h, cm.	a^2, mm ^{2}	a^2, average	$D - d$	Surface tension γ, dynes/cm.
30	3	0.1127	01191	0.2296			
	4	.1912	.1955	.2506			
	6	.1448	.1506	.2640			
	7	,1334	,1392	,2443	0.2471	0.456	0.552
20	3	.3398	.3462	.6675			
	4	.4713	.4756	.6097			
	6	3637	.3695	.6477			
	7	.3643	.3701	.6495	.6436	.638	2.012
10	3	.5019	.5083	.9800			
	4	.7163	.7206	.9238			
	6	.5730	.5788	1.0146			
	7	.5710	.5768	1.0123	.9827	.755	3.636
0	3	.6730	.6794	1.310			
	4	.9385	.9428	1.209			
	6	.7511	.7569	1.327			
	7	.7545	.7603	1.334	1.295	.851	5.400
−10	3	,8231	,8295	1.599			
	6	.9310	.9368	1.642			
	7	.9261	.9319	1.635			
	8	.6857	.6934	1 616	1.623	.926	7.364
−20	4	1.4182	1.4225	1.824			
	6	1.1080	1.1138	1.952			
	7	1.1240	1.1298	1.983			
	8	0.7902	0.7979	1.858	1.904	.979	9.134
−30	4	1 6522	1 6565	2.124			
	6	1 2705	1.2763	2.237			
	7	1.2793	1.2851	2 255			
	8	0.9128	0.9205	2.145	2.190	1.014	10.88
−40	3	1.2880	1.2944	2.496			
	6	1.3919	1.3977	2.450			
	7	1.4230	1.4288	2.508			
	8	1.0600	1.0677	2.488	2.485	1.037	12.63
−50	3	1.4060	1.4124	2.723			
	6	1.5908	1.5966	2.799			
	7	1.6164	16222	2.847			
	8	1.1881	1.1958	2.787	2.789	1.053	14.39

Internal Radius of Capillary Tubes

Tube No.	3	4	6	7	8
Radius, cm.	0.01928	0.01282	0.01753	0.01755	0.02330

and d the density of its saturated vapor. The values for these densities were obtained by plotting on large-scale cross-section paper the results obtained by the authors in a previous investigation,[9] and from the curve thus obtained, the density values for both liquid and vapor were read.

Discussion of Results

Much interest has been shown in recent years in the relations between surface tension, liquid and gaseous densities and internal pressures. Some years ago van der Waals,[10] by a theoretical consideration of the forces acting between the molecules of a liquid, developed the equation $\gamma = K(1 - T/T_c)^n$. In this equation γ is the surface tension at the absolute temperature T, n is an exponent having a value of about 1.2 for all non-polar liquids and T_c is the critical temperature of the liquid. The constant K is supposed to hold over a large temperature range and is characteristic of the liquid. As in most equations involving the surface tension, it fits the experimental values much better at temperatures well removed from the critical temperature.

Recently, Macleod[11] developed an empirical equation for the relation between the surface tension and the densities of a liquid and its saturated vapor. This equation, when put in the form $\gamma/(D - d)^4 = C$, represents the experimental results very well in most cases. Here D is the density of the liquid and d the density of its saturated vapor, while C is a constant characteristic of the liquid in question.

Another interesting equation is that proposed by Sugden,[12] which he writes in the form $D - d = D_0(1 - T/T_c)^{0.3}$. D_0 in this equation represents the density of the supercooled liquid at absolute zero.

By combining the equations of Macleod and Sugden, the following equation is obtained: $\gamma = C \times D_0^4(1 - T/T_c)^{1.2}$. This is evidently van der Waals' equation in such cases as the exponent n may be 1.2. It is perhaps interesting to note that van der Waals' constant K is equal to $C \times D_0^4$ and as C is equal to the ratio of the surface tension to the fourth power of the difference in density of the liquid and vapor, it is quite possible to make use of it in calculating the volume occupied by a molecule of the liquid.

From the surface tension measurements made during this investigation, it seems that van der Waals' equation gives the highest degree of accuracy when written in the form $\gamma = 72.8\ (1 - T/311.8)^{1.26}$. The exponent n was calculated from the readings at fifteen pairs of temperatures and the average was found to be 1.26. The value of K was determined at all temperatures at which surface tension measurements had been made, using

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[9] Quinn and Wernimont, THIS JOURNAL, 51, 2007 (1929).

[10] Van der Waals, *Z. physik. Chem.*, 13, 716 (1894).

[11] Macleod, *Trans. Faraday Soc.*, **19**, 38 (1923).

[12] Sugden, *J. Chem. Soc.*, 130, [Part 2] 1780 (1927).

the exponent 1.26. The average of these values, excluding the one obtained at 30°, was 72.8. The agreement between the observed values obtained in this investigation for the surface tension of liquid nitrous oxide and those calculated from the above equation is shown in Table III, while the observed and calculated values obtained from Verschaffelt's[13] work are given in Table IV for comparison.

Table III

Observed and Calculated Values for the Surface Tension of Nitrous Oxide Obtained in this Investigation

Temp, °C.	K	Observed	Calculated	Diff.	% diff.
30	49 3	0 552	0 816	$0 26	+47 8
20	69 3	2 01	2 11	+ .10	+ 4.9
10	73 0	3 64	3.63	− .O1	− 0 3
0	74.6	5 40	5.27	− .13	− 2 4
−10	76.2	7.36	7 03	− .33	− 4 4
−20	74.7	9.13	8 90	− .23	− 2 5
−30	73.0	10.88	10.84	− .04	− 0.4
−40	71.5	12.63	12.86	+ .23	+ 1.8
−50	70.0	14.39	14.95	+ .56	+ 0 9

Average percentage difference (disregarding sign) 2.6

NOTE.—Values obtained at 30" are not used in averages because this temperature is so near the critical temperature.

Table IV

Observed and Calculated Values for the Surface Tension of Liquid Nitrous Oxide Obtained by Verschaffelt

Temp, °C.	Observed	Calculated	Diff.	% Diff.
25	1 07	1 36	+0 29	+27.1
20	1.75	2 05	+ .30	+17 1
15	2 50	2 81	+ .31	+12 4
10	3 30	3 62	+ .32	+10 0
−25	10.10	10.40	+ .30	+ 3.0

Average percentage difference 13.8

NOTE.—These results seem to indicate that the constants as given by Verschaffelt could be changed so as to greatly improve the agreement between the calculated and observed values.

The Internal Pressure of Nitrous Oxide

No very satisfactory method for calculating internal pressure from surface tension measurements exists, in spite of the fact that one would expect this to be one of the best ways of dealing with the question. According to Hildebrand[14] the values of $\gamma/v^{1/3}$ are useful for indicating the relative internal pressures where v is the molal volume of the liquid. Calculating

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[13] "International Critical Tables," McGraw-Hill Book Co , Inc., New York, Vol. IV, p. 447.

[14] Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York 1924, p. 111.

the values for $\gamma/v^{1/3}$ at 20° for carbon dioxide and nitrous oxide, we get 0.355 and 0.528, respectively. Now if we arrange these compounds in the Hildebrand series according to the decreasing order here indicated, we find that carbon dioxide is the first member, then nitrous oxide, and after a big gap we come to nickel carbonyl. According to the theory of solubility this can only mean that carbon dioxide and nitrous oxide in the liquid state are poor solvents for the common solutes and that of the two compounds we would expect nitrous oxide to be the better.

Summary

1. Surface tension measurements of liquid nitrous oxide have been made over a temperature range of **30** to −50°.
2. The equation of van der Waals for the change of surface tension with a change of temperature, when put in the form of $\gamma = 72.S\ (1 - T/311.8)^{1.26}$ gave values for γ which were in fairly good agreement with those determined experimentally.
3. From the position of nitrous oxide in the internal pressure series of Hildebrand, it was predicted that it would be a poor solvent for the common solutes but that it was somewhat better than liquid carbon dioxide.

SALT LAKE CITY, UTAH

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE COAGULATION OF FERRIC OXIDE SOLS BY GAS BUBBLES[1]

BY HENRY M. STARK

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A ferric oxide sol of great purity has been prepared by C. H. Sorum[2] in this Laboratory. Due to its extremely low chloride content this sol has rather special properties. While making conductivity measurements on this sol Sorum observed that if streams of air bubbles were used as a stirring agent coagulation took place. Other gases were tried and the phenomenon seemed to be general. Since no mention had been made anywhere in the literature concerning the coagulation of colloid systems by gas bubbles, this phenomenon presented an interesting problem for investigation.

Coagulation of colloids such as ferric oxide is usually considered to be due either to destruction or neutralization of the charge on the particle by the

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[1] An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin. The problem was suggested by Dr. C. H. Sorum and carried out under the supervision of Professor J. H. Walton. The author wishes to express his indebtedness to Mr. A. G. Jacques for many valuable suggestions.

[2] Sorum, THIS JOURNAL, 50, 1263 (1928).

oppositely charged ion of the coagulating electrolyte or to destruction by dehydration of the orientation of the molecules of the stabilizing layer of dispersion medium. Coagulation of a colloid by gas bubbles, because of the obvious difference in the nature of the process, cannot be attributed to these causes. Several possible factors might be considered as the direct cause of the coagulation, *viz.* (1) the neutralization of the charge on the ferric oxide particles by that on the gas bubbles, (2) the increased frequency and force of collision of the sol particles due to the agitation produced by the gas bubbles, or **(3)** adsorption of the colloid into the interface gas–liquid with consequent surface concentration. These factors will be discussed in detail after the experimental results have been described. The influence of such factors as the presence of impurities or of free electrons in the gas used for coagulation was reduced to as nearly a minimum as possible in the experimental part and will be given no further consideration.

Experimental

The ferric oxide sol used in this work was prepared and purified according to the method outlined by Sorum. A large volume of sol was prepared at one time and stored in 24-liter pyrex flasks. The sol used in most of this work contained 2.98 g. of iron per liter. Its flocculation value was between 5.5 and **6.0** millimoles of sodium chloride per liter, which is abnormally low for ferric oxide sols. The sol was so stable that neither its iron content nor its flocculation value changed appreciably on standing for one year. The average size of the particles of this sol as determined by the ultramicroscope-count method with a slit ultramicroscope was $59\mu\mu$.[3]

Cataphoresis Measurements.—A rather surprising property of this sol was that the charge on the particle, obtained from measurements of velocity of cataphoresis, was not abnormally low. Using the apparatus described by Burton[4] a large number of measurements of velocity of cataphoresis were made. In order to obtain uniform values for the ascending and descending boundaries, it was necessary to produce what Mukherjee[5] calls a "uniform ionic environment." This was done by adding to the liquid to be used above the ferric oxide layer, small quantities of an equimolecular mixture of ferric chloride and hydrochloric acid until the conductivity of the liquid and of the sol were equal. The results obtained from these cataphoresis measurements are compiled in Table I.

These values were obtained by direct substitution into the equation of Helmholtz for the relation between particle charge and velocity of cataphoresis, $V = 4\pi nv/DX$, where V is the so-called zeta-potential, D is the dielectric constant of the liquid, n its viscosity, X the applied voltage and

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[3] Ayres, *J. Phys. Chem.*, *34*, *875 (1930)*.

[4] Burton, *Phil.* ***Mag.***, [6] 11, 425 (1906); [6] 11, 44 (1906).

[5] Mukherjee, *J. Ind. Chem. Soc.*, *5*, **593** (1928).

TABLE I

VELOCITY OF CATAPHORESIS OF FERRIC OXIDE PARTICLES

Cat. vel. in cm./hr.	Temp., °C.	Volts	Cm./sec./volt/cm.	Charge in millivolts
2.65	23.0	108	46.4×10^{-5}	61.6
2.72	23.4	106	48.5×10^{-5}	65.0
2.88	22.3	107	51.0×10^{-5}	69.0
2.68	23.1	107	47.4×10^{-5}	62.3
2.35	17.6	107	41.6×10^{-5}	62.0
			Average	63.98

v the velocity of movement of the particles. If, in the above formula, Debye's[6] correction for spherical particles is made, in which 6π is substituted for 4a, the values for zeta-potential would be 50% higher. The value of 64 millivolts agrees fairly well with values determined by other investigators; Whitney and Blake[7] give 42 millivolts while Burton[8] gives 73 millivolts. Neither of these investigators made any special effort to make a sol of great purity.

On the basis of the results given in Table I, it appears that the low chloride content of this sol does not materially reduce the charge of its particles and that therefore the very low flocculation value must be accounted for in some other way.

Method of Coagulation.—Inert gases, after being carefully purified, were emitted as streams of small bubbles at the bottom of 8-inch pyrex tubes each containing 40 cc. of the sol. The volume of gas passing through was measured by means of a calibrated flowmeter and the number of bubbles forming per minute was counted. From these two values the size of the bubble was determined. Various kinds of tubes were used to conduct the gas to the bottom of the tube of sol and to serve as an emission tip, but in the greater portion of the work described below capillary tubing with one millimeter bore was used. When the gas was passed through the sol at rates varying from 0.63 to 6.80 liters per hour, noticeable coagulation took place within two to four hours, but complete coagulation required twenty-four to thirty-six hours.

Samples were removed at arbitrarily chosen intervals and the degree of coagulation was determined by centrifuging the sample of sol to separate the coagulated from the uncoagulated portion. Centrifuging for ten minutes at 2300 r. p. m. served to throw the larger particles to the bottom to such an extent that the supernatant liquid was again clear. Longer centrifuging caused no further reduction in the iron content of the supernatant liquid. Also, the same centrifuge treatment of the original sol caused no settling.

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[6] Debye and Huckel, *Physik* Z., 25, 49 (1924).

[7] Whitney and Blake, THIS JOURNAL, 26, 1339 (1904).

[8] Burton, "The Physical Properties of Colloidal Solutions," Longmans, Green and Co., London, 2d ed., 1921, p. 143.

The iron content of the supernatant liquid was determined by titrating the reduced iron against potassium dichromate using diphenylamine as an inside indicator. In the calculation of the degree to which coagulation had taken place the iron content of the supernatant liquid after centrifuging was assumed to be proportional to the uncoagulated portion of the sol. This method of determining degree of coagulation is certainly open to criticism because of the "broom" effect of the larger particles sweeping down with them some of the smaller uncoagulated particles. It is doubtful, moreover, if the centrifuging would cause settling of aggregates only partially coagulated and containing two or three original particles. The values when obtained under constant conditions, however, do serve as an arbitrary measure of the extent of coagulation in the experiments described below.

Results

Effects of Different Gases.—Five different gases were used and the coagulating power of each determined. The values given in Table II indicate that the nature of the gas was not a very important factor except in the case of carbon dioxide, in which case the hydrogen-ion concentration of the sol was changed by the presence of the gas. The values are not the same for all gases but do not show the wide variations that are obtained for the coagulating action of electrolytes. That the reason for the failure of carbon dioxide to cause coagulation lay in its effect on the hydrogen-ion concentration was established by the following experiment. By means of a quinhydrone electrode apparatus for determination of hydrogen-ion concentrations, it was shown that the PH of a sol saturated with carbon dioxide was about 4.3 at room temperature. Different members of a series of tubes of sol were brought to different PH values by adding varying quantities of molar acetic acid and molar sodium acetate. The samples having a PH value farther toward the alkaline side than 4.6 were very unstable toward air bubbling, while those with a PH lower than 4.6 were not coagulated by air bubbles. The PH of the sol alone was about 6.4. It appears, therefore, that carbon dioxide in dissolving in the water and lowering the PH from about 6.4 to **4.3** causes the sol to pass from the region of instability toward gas bubbling to that of great stability.

TABLE II

COAGULATING POWER OF VARIOUS GASES

Gas	Fe precipitated by 1 liter of gas, g.
Oxygen	453×10^{-7}
Nitrogen	273×10^{-7}
Air	317×10^{-7}
Hydrogen	428×10^{-7}
Carbon dioxide	Caused no coagulation

As stated above, the gas was carefully purified before it passed into the tube of sol. However, in order to eliminate such factors as impurities in the gas or free electrons from consideration as possible causes of the coagulation, the following experiment was carried out. A given volume of gas was passed through a series of six tubes containing equal quantities of sol and arranged in such a manner that the gas emerging from the top of one tube was led to the bottom of the next. After the gas had passed at the rate of 0.29 liter per hour for thirteen hours, samples were withdrawn, centrifuged and the supernatant liquid analyzed. Table III shows that no loss in coagulating power of the gas took place as it passed through the series of six tubes. Since in passing through such a series of tubes impurities and free electrons would be largely absorbed in the first members of the series, we may infer from these data that these two factors are not responsible for the coagulating action of the gas.

TABLE III

SHOWING CONSTANT COAGULATING POWER OF THE GAS

Tube	Fe precipitated, g.	Fe per liter after bubbling and centrifuging, g.
1	0.0060	1.82
2	.0056	1.87
3	.0056	1.87
4	.0063	1.81
5	.0052	1.86
6	.0061	1.83

Influence of Non-Electrolytes.—Janek and Jirgensons[9] found that in low concentrations, alcohols decrease the stability of ferric oxide sols but when present in higher concentrations they increase the stability, as measured by the quantity of electrolyte required to cause complete precipitation in an arbitrarily chosen interval. Alcohols of high molecular weight had greater influence on stability than lower members of the alcohol series. In this investigation a study was made of the influence of various alcohols on the stability of ferric oxide sol toward gas bubbling. Ethyl and methyl alcohols had very little effect on the amount of colloid precipitated in a specified time, but higher members affected stability more markedly. The relationship between proportion of alcohol present and stability of the sol was similar to that found by Janek and Jirgensons. In Table IV are given the results obtained when small quantities of isopropyl, isobutyl and *n*-butyl alcohols were added to 40-cc. portions of sol just previous to coagulation by bubbling gas through them. Equal volumes of gas were passed through the different tubes. The data indicate that very small proportions of alcohol cause sensitization but that this sensitizing action decreases as more alcohol is added.

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[9] Janek and Jirgensons, *Kolloid-Z.*, 41, 40 (1927).

TABLE IV

EFFECT OF ALCOHOLS ON STABILITY OF FERRIC OXIDE SOL TOWARD GAS BUBBLING

Isopropyl alcohol		Isobutyl alcohol		n-Butyl alcohol	
Volume per cent. of alcohol added	Iron precipitated, %	Volume per cent. of alcohol added	Iron precipitated, %	Volume per cent. of alcohol added	Iron precipitated, %
0.0	10.0	0.0	3.4	0.0	30.4
0.2	30.0	0.2	25.8	0.2	49.4
1.0	28.1	0.4	28.0	0.4	67.3
4.0	17.0	1.0	17.0	1.0	54.0
		2.0	9.0	2.0	47.2
		4.0	5.5	4.0	37.0

Influence of Electrolytes on Coagulation by Gas Bubbles.—Investigations carried out by Sorum and Judd[10] in this Laboratory have shown that the specially purified sol used in this work may be coagulated by a lower concentration of electrolyte than ordinary ferric oxide sols. In this investigation it has been shown that coagulation of this ferric oxide sol takes place in still lower concentrations of electrolyte when streams of gas bubbles are passed through the sol. Determinations were made of the minimum concentrations in millimoles per liter of various electrolytes required to cause complete coagulation of the sol during twenty hours of gas bubbling. The gas was passed through the tubes of sol at the rate of 0.29 liter per minute. Complete coagulation was assumed to have taken place when after twenty hours' bubbling and ten minutes' centrifuging there remained less than 1% of the original iron of the sol in the supernatant liquid. In Table V this minimum concentration is called the "coagulation value."

TABLE V

COAGULATION VALUES FOR VARIOUS ELECTROLYTES

Electrolyte	Coagulation value	Flocculation value (Judd)	Electrolyte	Coagulation value	Flocculation value (Judd)
NaCl	2 0	3.8	Na_2SO_4	0.10	0.46
KCl	4.0	13.0	K_2SO_4	.30	.59
$BaCl_2$	10 0	...	$K_2Cr_2O_7$	.375	.399
$MgCl_2$	5.0	...	$MgSO_4$	.10	...
$Th(NO_3)_4$	Above 300	...	Na_3PO_4	.025	...
$ThCl_4$	..	395 0		.050	...
$AgNO_3$	10.0	47.0	$K_3Fe(CN)_6$	.05	.084
$NaNO_3$	2.5	56 0	$K_4Fe(CN)_6$	.025	.033
$Al(NO_3)_3$	62.5	182.0			

The values given in the third column are the flocculation values, *i. e.*, the concentrations of electrolyte required to cause complete coagulation in two hours without agitation, obtained by Judd in an investigation of this sol. It is obvious that the concentrations of electrolyte required to cause complete coagulation were uniformly lower when the sol was stirred with

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[10] Judd and Sorum, THIS JOURNAL, 52, 2598 (1930).

gas bubbles than when it was at rest. The amount of gas bubbling applied in this experiment was sufficient to coagulate approximately 25% of the particles of the sol in the absence of electrolyte. The values given in the second column represent the additive effects of gas bubbling and addition of electrolyte, which accounts for their being uniformly lower than the flocculation values given in the third column.

Coagulation Velocity.—Smoluchowski[11] developed the following equation to represent the decrease in the number of particles of a sol during the process of coagulation

$$n = \frac{n_0}{1 + 4\pi D r n_0 t}$$

where n is the total number of particles present at any time t, n_0 is the number originally present, D is the diffusion constant and r is the radius of the sphere of attraction of the particles. For the number of *single* particles present after a time t, the expression becomes

$$n_1 = \frac{n_0}{(1 + 4\pi D r n_0 t)^2}$$

or setting $4\pi Dr = $ k the expression becomes

$$n_1 = \frac{n_0}{(1 + k n_0 t)^2} \text{ or } k = \frac{1}{t}\left(\sqrt{\frac{n_0}{n_1}} - 1\right)$$

Smoluchowski is of the opinion that the laws of rapid coagulation should also apply to the phenomenon of slow coagulation except that there should be inserted a factor in the above expression, representing the proportion of the collisions between particles which are fruitful in producing coagulation. Freundlich and Basu[12] found that the decrease in the number of particles of copper oxide sol could be calculated from the Smoluchowski equation.

Coagulation velocity curves have been obtained for this ferric oxide sol in the presence of various electrolytes at different concentrations. The curves obtained by using potassium sulfate in varying concentrations are shown in Fig. 1. Curves for other electrolytes were similar to these except that ions of higher valence caused more rapid coagulation as is shown by the results recorded in Table V. Values of k were obtained by using the Smoluchowski equation. The iron content of the supernatant liquid at time t was assumed to be proportional to the number of single particles n_0. These values of k for arbitrarily chosen intervals of time are given in Table VI.

It will be seen from this table that for low concentrations of electrolyte the coagulation velocity increases slowly with increasing electrolyte concentration, but for higher concentrations the velocity increases rapidly. This is shown graphically in Fig. 2, where the log, of (k × 100) is plotted against the concentration of electrolyte. It is evident from this figure that

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[11] **Smoluchowski,** *Z. physik.* Chem., 92, 129 (1917).

[12] **Freundlich and Basu,** *ibid*, 115, 203 (1926).

TABLE VI

COAGULATION VELOCITY CONSTANTS FOR SOL CONTAINING K_2SO_4

Hours of agitation	Values of k at K_2SO_4 concentrations indicated concentrations given in millimols per liter 0.0	0.02	0.04	0.06	0.08	0.10
5	0.0126	0.014	0.014	0.018	0.045	0.29
10	.012	.014	.015	.018	.055	.39
15	.012	.014	.015	.019	.070	
20	.013	.014	.015	.020	.090	
25	.013	.015	.016	.022		
30	.013	.015	.017	.024		
40	.015	.017	.020	.031		

for lower concentrations of electrolyte a linear relation exists between the concentration of electrolyte and the logarithm of the coagulation velocity constant. This relation was expressed by Schalek and Szegvari[13] in the form of the equation

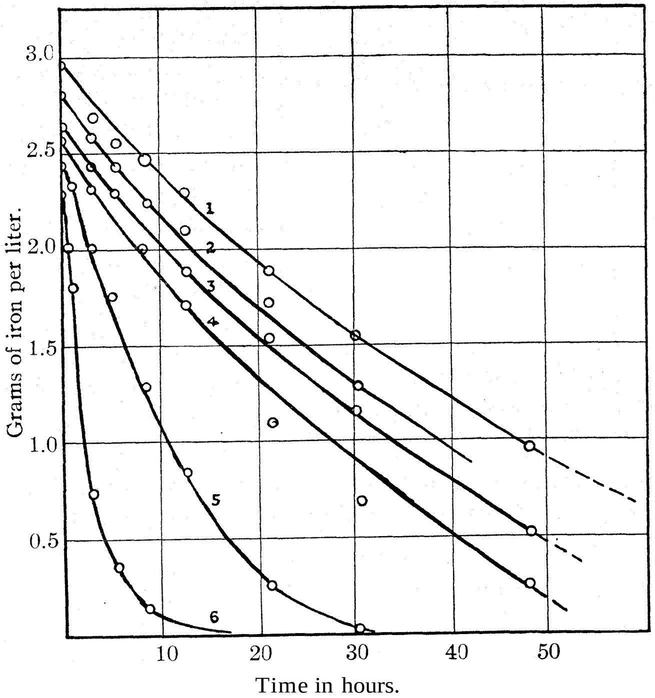

Fig. 1.—Influence of potassium sulfate on the velocity of coagulation of ferric oxide sols by gas bubbles. Coagulation velocity curves for: 1, sol alone; 2, sol containing 0.02 mml. per liter; 3, 0.04; 4, 0.06; 5, 0.08; 6, 0.10.

$$\log k = nc - l$$

where n and l are new constants. Freundlich and Basu[12] found that this

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[13] Schalek and Szegvari, Kolloid-Z., **33,** 326 (1923).

equation was valid for the coagulation of the copper oxide sol agitated by a mechanical stirrer.

In an effort to gain some knowledge concerning the mechanism of this coagulation phenomenon a study was made of the influence of such factors as height of column, rate of bubbling gas through the sol, size of bubble and others. The influence of the height of the column through which the gas was bubbled is shown in Table VII.

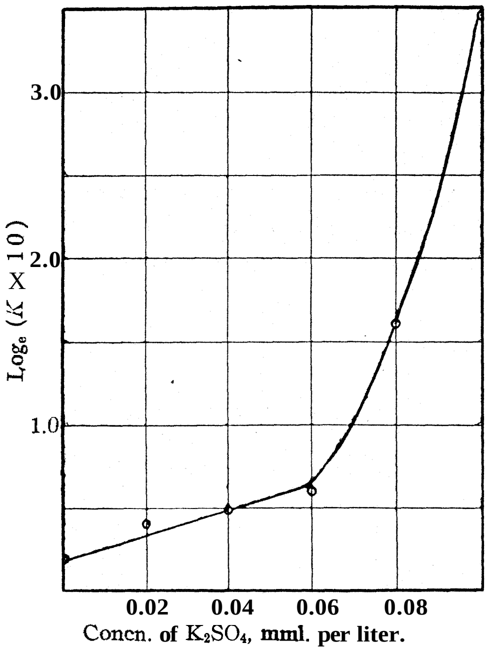

Fig. 2.—Relation between concentration of electrolyte and coagulation velocity constant.

A constant amount of gas was passed through each of the four tubes. It appears from these data that the height of the column influences the amount of coagulation taking place only to the extent that it affects the volume of liquid through which the gas passes. The total amount of sol coagulated in the above series was roughly proportional to the volume of sol present.

Rate of Flow of Gas.—The influence of the rate at which the bubbles of gas were passed through the tube of sol is shown in Table VIII.

These data indicate that up to a certain point increasing the rate of flow of the gas increases the rate at which the sol is coagulated, but that beyond

TABLE VII

INFLUENCE OF HEIGHT OF COLUMN ON AMOUNT OF COAGULATION

Sol, cc.	Height of column. cm.	Fe per liter after agitation by gas bubbles, g.
140	45	2.25
100	30	2.08
60	15	0 95
20	5	0 51

TABLE VIII

INFLUENCE OF THE RATE OF FLOW OF THE GAS ON ITS COAGULATING ACTION

Rate of flow in liters per hour	Fe precipitated by 1 liter of gas, g.	Rate of flow in liters per hour	Fe precipitated by 1 liter of gas, g.
0.63	0 052	10.63	0 018
1.06	.060	21.2	.010
2.51	.104	31.8	.009
6 80	035		

this point a further increase in rate of flow causes a decrease in the coagulating power of the gas.

Size of Bubble.—Variations in the size of the bubble such as were produced by the use of tips ranging from 1 to 17 millimeters in diameter caused no appreciable difference in the rate of coagulation.

Mechanical Agitation.—The sol was coagulated by any form of mechanical agitation. Thus, shaking vigorously, either in the presence of air or in a tube from which the air above the sol had been removed, caused coagulation to take place at a rate approximately the same as with gas bubbles. Stirring with a glass stirrer in the absence of carbon dioxide caused coagulation. The same forms of coagulation velocity curves were obtained for stirring in this manner as when the bubbling method was used.

Discussion of Results.—The coagulation phenomenon described in the preceding pages might appear to be caused by one or more factors, such as those mentioned in the introductory paragraphs of this article. The suggested causes of the coagulation mentioned are discussed below in the light of the experimental evidence presented.

(1) Neutralization of the Charge on the Colloid by the Charge on the Bubble.—The work of a large number of investigators supports the view that bubbles of inert gases suspended in water are negatively charged. Lenard[14] found that at the bottom of waterfalls the water or mist is positively charged and the air through which it has fallen is negatively charged. Thomson, McLean and Galt[15] and later Coehn and Mozer[16] by means of the quadrant electrometer, measured the charge produced by bubbles of inert gases as they rose through water and solutions of electrolytes. McTaggart[17] measured the charge on gas bubbles while they were immersed in a liquid by observing the rate of cataphoresis of small bubbles in water and solutions of electrolytes and non-electrolytes. He showed that all the inert gases which came under his investigation carried in water a negative charge, but that the magnitude and even the sign of this charge might be changed by the addition of small quantities of electrolytes. Also, the charge could be lowered by the addition of small quantities of alcohols and other non-electrolytes which lower the surface tension of water. Undoubtedly the electric charges encountered in these two instances are not of identical origin, and any charge gained by the bubbles in the experiments carried out in this investigation must be attributed to the same cause as in the case of McTaggart's work. The results obtained by adding small quantities of alcohols to the sol previous to coagulation, which are summarized in Table IV, indicate that the coagulation phenomenon here observed is not due

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[14] Lenard, *Ann. Physik,* [3] 46, *584* (1892).

[15] Thomson, McLean and Galt, *Proc. Roy. Soc.* (London), *57,* **335** (1895).

[16] Coehn and Mozer, *Ann. Physik,* [4] *43, 1048* (1914).

[17] McTaggart, *Phil.* Mag., [6] 27, 297 (1913); [6] 28,367 (1914); 44, 386 (1922).

primarily to a neutralization of the charge on the colloid by that on the gas bubble; for as McTaggart has shown, the addition of small proportions of alcohols to a liquid continually lowers the negative charge on *a* bubble of inert gas suspended in the liquid, which would decrease its power to coagulate a positively charged colloid. In this investigation, however, the addition of small amounts of alcohols actually caused greater amount of coagulation, The influence of the charge on the bubble probably is overshadowed by some other stronger factor.

(2) Coagulation **by** mechanical agitation produced **by gas bubbles,** in spite of its apparent feasibility, is probably relatively unimportant. The bubbles used in this work were relatively large (average, 0.1 cc.) and moved through the sol rather sluggishly. Under these conditions definite flow portions would be set up in which both water and sol particles move in a direction governed by the resultant of forces acting on the various discrete portions produced by the haphazard agitation of the gas bubbles. In order for the agitation to produce the increased frequency and force of collisions necessary to cause coagulation, it would be necessary for the particles of one flow portion to meet those of another flow portion going in an opposite direction; but the only place where two oppositely directed flow portions can meet is at the edges where the particles are moving at a very slow rate in comparison with the rate nearer the center of the flow portion. Collisions between particles in the same flow portion are unlikely because all are moving in the same direction.

The results obtained in the investigation substantiate the statements made above to the effect that mechanical agitation is not the chief factor in the coagulation phenomenon by gas bubbles. Thus variation in two factors which influence the intensity of agitation, *viz.*, the height of the column and the rate of bubbling, failed to give proportionate variations in coagulation. In Table VII it is shown that the iron content of the supernatant liquid increased with the height of the column. It may appear from this that coagulation increased with decreasing height of column and, therefore, with increasing agitation, but when account is taken of the fact that the volume of sol also increased with increasing height of column, it is apparent that approximately the same total quantity of sol was coagulated in each case. Again in Table VII the amount of coagulation decreases with increase in the rate of bubbling over most of the range. If coagulation were due primarily to mechanical agitation, increase in rate of bubbling would give rise to increased coagulation.

(3) Adsorption of the Colloid into the Interface Gas–Liquid with Consequent Concentration.—It is well known from the work of McTaggart that bubbles of inert gases suspended in solutions of electrolytes adsorb on their surfaces the ions present in solution. In like manner colloids are adsorbed from dilute sols, such as those of thorium hydroxide. McTaggart

obtained experimental evidence of a relation between curvature of the surface of the bubble and its adsorptive power. Kenrick[18] long ago worked out the potential difference relations for the interface gas solution and found that adsorption of anions was the cause of the potential difference between the two phases. He also showed that the potential difference was independent of the nature of the gas. Numerous other references might be cited in support of the view that ions and colloid particles are adsorbed on the surface of gas bubbles.

The phenomenon described above of the coagulation of a positively charged sol by gas bubbles might be attributed to adsorption at a gas–liquid interface as described above. We might picture the coagulation process as taking place in the following manner. The bubble in rising sluggishly through the sol adsorbs particles of colloid, carrying them to the surface of the liquid where the bubble collapses. The concentration of colloid particles in the interface gas–liquid at the surface of the bubbles is greater than in the remainder of the liquid and when these bubbles burst there is formed a very thin layer of liquid containing a much higher concentration of colloid particles. In these local areas at the upper surface of the sol, the concentration exceeds that at which the sol is stable and coagulation takes place by ordinary kinetic methods.

The data obtained in this investigation are in substantial agreement with the explanation of coagulation outlined above. Thus according to this view we would expect all inert gases to have approximately the same coagulating power, for the work of McTaggart and of Kenrick cited above and of Frumkin[19] indicates that adsorption at the surface of gas bubbles and hence the charge on the bubble are independent of the nature of the gas. The values given in Table II for the relative effects of different gases in coagulating the sol indicate that no wide differences exist for the inert gases. Gases exerting a chemical action come under a different category and undoubtedly show wide differences in their action toward this sol such as are shown in Table V to exist for electrolytes. The fact that the gas loses none of its coagulating power in passing through a series of tubes shown by the data in Table III would be expected as a result of the proposed mechanism of coagulation.

The effect of alcohols on the coagulation of ferric oxide by gas bubbles is similar to their effect on coagulation by electrolytes, *i. e.*, small quantities cause increased coagulation while larger amounts cause stabilization. Explanations offered for this anomalous effect of alcohols are not wholly concordant. In case of coagulation by gas bubbles the first small addition increases coagulation probably by increasing the size of the bubble and hence the adsorbing surface due to the decrease in surface tension of the liquid

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[18] Kenrick, *Z. physik. Chem.*, **19**, 625 (1896).

[19] Frumkin, *ibid.*, **109**, 34 (1924).

caused by the addition of the non-electrolyte. Further addition of alcohol while lowering the surface tension still more decreases the specific adsorption of the liquid–gas interface and in this manner decreases the amount of colloid carried to the surface to become coagulated.

In case of coagulation by gas bubbles in presence of small quantities of electrolytes, the colloid is sensitized by the electrolyte and coagulation takes place in the same way as outlined above. We also should expect coagulation to take. place at a lower electrolyte concentration when gas bubbles are passed through than when they are not. The coagulation values given in Table V indicate the additive effect of electrolyte and coagulation by adsorption on the gas bubbles.

The data obtained in studies on velocity of coagulation support the view that the relation of Smoluchowski, which was originally developed for a sol at the isoelectric point, holds also for this sol which still has considerable charge on its particles. Freundlich and Basu[12] have shown that copper oxide sol when agitated by a glass stirrer coagulates in such a way as to follow the Smoluchowski equation. The velocity constants given in Table VI for coagulation of ferric oxide in presence of small quantities of potassium sulfate are undoubtedly larger than would have been obtained with no gas bubbling and with the same electrolyte concentration since the coagulation process is the combined effect, first, of lowering of zeta-potential by the electrolyte and thus increasing the frequency of collision of the particles and, second, of adsorption of the particles in the gas–liquid interface and subsequent concentration of the sol particles at the surface of the liquid.

Mechanical agitation such as shaking and stirring causes the formation of large areas of gas–liquid interface on which temporary adsorption and concentration of particles beyond the limits of stability take place and in this way bring about coagulation.

Summary

1. Experiments have been carried out on the coagulation of ferric oxide sol by the following gases: oxygen, nitrogen, hydrogen, air and carbon dioxide.

2. The influence of various electrolytes and non-electrolytes on the coagulation by air bubbles has been determined.

3. Coagulation velocity studies have been made and the Smoluchowski equation for rapid coagulation found to hold. Also, the relation of Schalek and Szegvari was found to hold over a limited range of concentration of electrolyte.

4. An explanation concerning the mechanism of the coagulation process has been offered and discussed in the light of the data obtained.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

CHAIN REACTIONS PRODUCED BY LIGRT AND BY ALPHA RADIATION[1]

BY HUBERT N. ALYEA[2]

RECEIVED MARCH 31, 1930 PUBLISHED JULY 3, 1930

"Ion cluster" mechanisms, postulated for reactions taking place under alpha particle bombardment, could not explain the hydrogen–chlorine reaction.[3] Here the secondary step was an atomic chlorine chain, as in the corresponding photochemical reaction.* Inasmuch as no other photochemical chain reactions had ever been studied under alpha particle bombardment, such a comparison seemed timely, to ascertain how generally a chain mechanism, instead of ion clustering, might succeed the initial process of alpha particle ionization. The criterion for such a chain process would be a large number of molecules reacting per ion pair produced, and this, in turn, should be compared with the corresponding photochemical yield.

This was done for the reactions of (1) the hydrogen–chlorine **combination,**[4] and (2) the synthesis of phosgene from carbon monoxide and **chlorine.**[5] The reader is referred to the citations, where experimental methods and results for these two reactions under both light and alpha radiations are discussed in detail.

(3) The Chlorination of Benzene.—C. P. benzene saturated with chlorine was sealed in a tube together with a thin capillary containing a known amount of radon. Nitrogen was bubbled into the tube before sealing, although the benzene still contained a certain amount of dissolved atmospheric oxygen which was not removed. The tube was shaken momentarily to break the capillary, which distributed radon throughout the solution, and it was then allowed to stand in the dark for several hours, by which time all of the chlorine had reacted. Blank runs were likewise made. The formation of hexachlorobenzene was measured by titration of the free chlorine with standard thiosulfate solution[6] at the beginning and conclusion of a run. A typical run with 0.0046 curie of radon gave 1.4 millimoles of chlorine in 20 cc. of benzene reacted in one hour. This represents a total of 6.06 X 10^{20} (= the number of chlorine molecules in one millimole of

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[1] I am indebted to Professor S. C. Lind for his kindly interest and helpful suggestions during this research.

[2] National Research Fellow.

[3] S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," The Chemical Catalog Co., New York, 1928, American Chemical Society Monograph No. 2, 2d ed., p. 139.

[4] S. C. Lind and R. S. Livingston, THIS JOURNAL, 52, 593 (1930). See also F. Porter, D. C. Bardwell and S. C. Lind, ibid., **48,** 2603 (1926).

[5] H. N. Alyea and S. C. Lind, *ibid.*, 52, 1853 (1930).

[6] **A.** Slator, *Z. physik.* Chem., 45,540 (1903).

chlorine) × 1.4/60 × 60 × 3 (since three chlorine molecules are consumed to give one molecule of hexachlorobenzene) = 7.9 × 10^{16} molecules formed per second = M. While Rn and RnA attain equilibrium quickly and had exerted practically full ionizing activity during the one-hour reaction period, RaC′ was able to contribute only about 15% of the ionization it normally causes at equilibrium. This effect is allowed for by assuming only 2.15 instead of 3.0 sets of alpha particles from the original radon. Using these values, N = the number of alpha particles per curie of radon × radon concentration in curies × the number of ions produced by one alpha particle = $(2.15 \times 3.72 \times 10^{10}) \times (0.0046) \times (2.37 \times 10^5 \times 1.30)$, assuming the specific ionization of the mixture to be 1.30; or $N = 1.1 \times 10^{14}$. Therefore

$$\frac{M_{C_6H_6Cl_6}}{N_{C_6H_6Cl_6 + C_6H_6 + Cl_2}} = 7.9 \times 10^{16}/1.1 \times 10^{14} = 720$$

In similarly conducted experiments by Luther and Goldberg,[7] a minimum photochemical chain length of 75 is indicated by the fact that the photochemical rate is that many times slower in the presence of oxygen, an inhibitor.[8] Prom the nature of the induction period which they obtained, it can be conjectured that the actual photochemical chain length is probably rather large, although no definite value can be assigned to it in this note.

(4) Oxidation of Sodium Sulfite in Solution.—The photochemical measurements have been previously described[8] and consisted in shaking 20 cc. of 0.6 molar aqueous sulfite solution in a bottle filled with oxygen. The sulfite disappearing was determined titrimetrically at the end of the shaking period. For the alpha-particle reaction the experimental procedure was identical, but in addition a thin capillary containing a known quantity of radon was placed in the sulfite solution. Immediately upon beginning to shake, the capillary broke and distributed the radon throughout the system. In the absence of radon 1.40 millimoles of sodium sulfite oxidized in five minutes; 0.0043 curie of radon increased the rate 0.20 millimole. The calculation of M/N carried out as above for the chlorination of benzene yields a chain length greater than 5000 molecules per ion pair produced.

Exponentially following each yield in the table is a reference to the original source of the value quoted. The yield 200,000 has no great significance in itself, since it depends on the purity of the gases. Of greater importance is, that simultaneous measurements on the same gas mixture give a ratio of $M/N{:}M/h\nu$ of 1:1. The same ratio is also obtained for the phosgene synthesis. Here, an additional factor makes the absolute value of 5000 of still less importance: the yield depends on the intensity of the radiation, and under more favorable conditions has been as high as 85,000 molecules

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[7] R. Luther and E. Goldberg, *Z. physik. Chem.*, 56, 43 (1906).

[8] H. N. Alyea and H. J. Backstrom, THIS JOURNAL, 51, 90 (1929).

TABLE I

RESULTS OF EXPERIMENTS

Reaction studied	*Calculation of M/N values on the basis of*	*M/N Alpha reaction*	*N/hν light reaction*
(1) $H_2 + Cl_2 \longrightarrow 2HCl$	$M_{HCl}/N_{H_2 + Cl_2}$	200,000[4]	200,000[4]
(2) $CO + Cl_2 \longrightarrow COCl_2$	$M_{COCl_2}/N_{CO + Cl_2}$	5,000[5]	5,000[5]
(3) C_6H_6 (liq.) $+ 3Cl_2 \longrightarrow$			
$C_6H_6Cl_6$	$M_{C_6H_6Cl_6}/N_{C_6H_6Cl_6 + Cl_2 + C_6H_6}$	$>$ 700[9]	large[7]
(4) Na_2SO_3 (soln.) $+ \frac{1}{2} O_2 \longrightarrow$			
Na_2SO_4	$M_{Na_2SO_4}/N_{H_2O + Na_2SO_3 + Na_2SO_4}$	$>$ 5,000'	100,000[8]

M/N = number of molecules formed per ion pair produced.
$N/h\nu$ = number of molecules formed per quantum absorbed.

per ion pair. The values 700 and 5000 are only semi-quantitative, the impurities in the materials and experimental errors being much greater in the alpha-particle runs. For this reason, the M/N values have been calculated for Reactions **3** and 4 by assuming that all questionable factors are operating in that direction which would lead to shorter chains. Thus, in calculating N, it is assumed that ionization not only of the reactants, but of the products as well[10] leads to reaction. The M/N value so derived represents a minimum chain length; more accurate determinations with carefully purified materials might give a much *larger* yield per ion pair (and undoubtedly would), but certainly no *smaller.*

The results point undeniably to the fact that in these four photochemical chain reaction, alpha-particle bombardment gives rise to chains instead of ion cluster reactions. No doubt many other photochemical chain reactions would give analogous results, and we wish in particular to emphasize this as another method for the identification and study of chain reactions.

MINNEAPOLIS, MINNESOTA

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[9] Values taken from data in this paper.

[10] Compare the decomposition of hydrogen iodide in aqueous solutions by radon, S. C. Lind, Le Radium, 8, 289 (1911); and by β- and γ-rays, Kailan, *Sitzb. Akad. Wiss. Wien,* ***121,*** 1351 (1912).

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE DECOMPOSITION OF MALIC ACID BY SULFURIC ACID

BY HARRY R. DITTMAR

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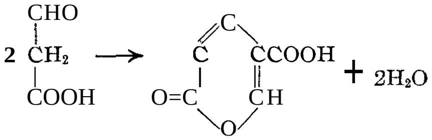
Although Dobereiner[1] showed that carbon monoxide resulted from the decomposition of malic acid by concentrated sulfuric acid, it remained for v. Pechmann[2] to demonstrate that the reaction was quantitative and that α-pyrone-β′-carboxylic acid was also formed in accordance with the equations

$$HOOCCH_2CHOHCOOH \longrightarrow CO + H_2O + HOOCCH_2CHO$$

then



Whitford[3] studied this reaction quantitatively, and found that it was an apparent first-order reaction, had a very high temperature coefficient and was inhibited by sodium, potassium and silver sulfates, acetic acid and dimethylpyrone. This investigator proposed an explanation for the mechanism of the reaction by postulating an unstable intermediate addition compound between malic and sulfuric acids, while the action of inhibitors was explained on the basis of a theory of negative catalysis formulated by Taylor.[4] It was suggested that an inhibitor such as dimethylpyrone, for instance, was effective because it combined with the sulfuric acid and so prevented the latter compound from taking part in the reaction.

The present investigation was undertaken with the object of making a study of the action of several more inhibitors at different temperatures and at more than one concentration in order to obtain the temperature coefficients of the inhibited reaction, which, in turn, might be used in gaining an insight into the mechanism of the inhibition.

Experimental

Preparation and Purification of Materials

Malic Acid.—Inactive malic acid obtained from Kahlbaum was used after being dried at 75° at a pressure of 2 mm. of mercury. The acid melted at 130.8° (corr.).

Sulfuric Acid.—One hundred per cent. sulfuric acid was prepared by adding C. P. 95% sulfuric acid to a given quantity of fuming sulfuric acid until the resulting solution melted at 10.42°, a value which was in good agreement with that obtained by other

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[1] Dobereiner, *J. für Chem. Phys.*, *26*, **276** *(1819)*.

[2] V. Pechmann, *Ber.*, **17**, **936 (1884)**.

[3] Whitford, THIS JOURNAL, 47, **953 (1925)**.

[4] Taylor, J. *Phys. Chem.*, **27**, **322 (1923)**.

investigators. A chemical analysis was also made by dissolving samples weighed by means of a weighing pipet in water and precipitating as barium sulfate. Two determinations gave 100.08 and 100.15% of sulfuric acid.

Phenol.—C. P. phenol (Mallinckrodt) was twice redistilled. The fraction which boiled at 182° (corr.) was used.

p-Cresol.—p-Cresol labeled "practical" (Eastman) was twice redistilled. The fraction which boiled at 201° (corr.) was employed.

Phosphoric Acid.—Pure crystalline orthophosphoric acid was used which melted at 42.3°. This acid was prepared by Mr. **A.** Weber in this Laboratory.

The other substances, which were the purest obtainable from reliable sources, were carefully dried before being used. The ethyl alcohol was dehydrated by calcium oxide in the usual manner. Acetophenone was redistilled. All of the solids with a melting point above 75° were dried at that temperature under a pressure of 2 mm. of mercury except benzophenone, which was dried at 35° at this pressure. All of the substances used were preserved in desiccators over phosphorus pentoxide.

Apparatus and Method of Procedure

The speed of the decomposition of malic acid by sulfuric acid was followed by measuring the volume of carbon monoxide which was evolved in various time intervals. The apparatus, including the mechanical agitator, reaction flasks and burets was identical with that used in a study of the decomposition of triphenylacetic acid by sulfuric acid and has been described in detail in another communication.[5] In each decomposition a 50-mg. sample of malic acid was decomposed in 10 cc. of sulfuric acid. This amount liberated about 9.51 cc. of carbon monoxide at 30° and 732.5 mm.

Solutions of various substances in 100% sulfuric acid were prepared by adding definite weights of the solutes to 50-cc. tightly stoppered Erlenmeyer flasks into which were weighed calculated quantities of 100% sulfuric acid. In cases where the solutes were hygroscopic, they were weighed into the flasks by means of either a weighing bottle or a weighing pipet.

Results

Decomposition by One Hundred Per Cent. Sulfuric Acid.—In accordance with Whitford's[3] results, the data obtained by measuring the volume of carbon monoxide evolved at various intervals of time when substituted in the equation for a monomolecular reaction, $K = (2.303/t) \log [a/(a - x)]$, gave constant values of K for any one decomposition. The first reading was usually taken after approximately 20% of the malic acid had been decomposed. This was necessary in order to allow the malic acid to first dissolve in the sulfuric acid. The carbon monoxide in cc. evolved between the first reading and the end of the reaction was substituted for a in the equation and the volume from the initial reading to that at time t as x.

The value of the velocity constant was constant until the reaction was 80–90% complete, after which k had the tendency to decrease. The values of $K \times 10^3$ obtained in a typical decomposition were: 30.6, 31.2, 31.1, 31.2, 30.8, 30.7, 30.5, 30.6, 30.6, 30.4, 30.2, 30.4. These constants were calculated from the data obtained between 27 and 83% of the

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[5] Dittmar, *J. Phys. Chem.*, 33, **533** (1929).

reaction. The value of the velocity-constant for any particular decomposition was taken as the average value of K $\times$ 10^3 between 25 and 70% of the reaction. In order to conserve space, only the mean value of the velocity constant is given in the subsequent tables rather than all of the data obtained from one decomposition. In studying the speed of decomposition under a given set of conditions, duplicate or more runs were always made, and the value of the velocity constant reported in the tables represents the average of the determinations. The check decompositions usually did not differ by more than 3%.

The absolute values of K were found to be somewhat higher than those obtained by Whitford.[3] For instance, K X 10^3 was found to be 11.1, 47.1 and 182.0 for 20, 30 and 40°, respectively, whereas Whitford obtained values of 7.6, 28.7 and 106.0 for the same temperatures. This discrepancy may have been caused by a slight difference in the experimental procedure. In this investigation the solid malic acid, contained in a small glass capsule, was introduced directly into the sulfuric acid at the moment agitation of the reaction flask was begun; while in the other case the malic acid was first dissolved in the sulfuric acid, after which samples were pipetted into the reaction flasks and allowed to stand in the thermostat for about fifteen minutes before the experiment was begun. However, the temperature coefficient between 30 and 40° checks the latter's value quite well although the temperature coefficient between 20 and 30° is somewhat higher. These results are given in Table I.

TABLE I

EFFECT OF TEMPERATURE UPON THE RATE OF DECOMPOSITION OF MALIC ACID BY 100% SULFURIC ACID

Temp, °C.	$K \times 10^3$	Temp. coeff.	Crit increment
20	11.1		
		4 24	25,510
30	47.1		
40 (calcd.)	182 0	3.86	25,480
25	23 8		
		3.92	25,000
35	93 2		

The speed of the decomposition at 40° was so great that reliable data could not be obtained. The value of K $\times$ 10^3 at this temperature was obtained by extrapolation from the curve obtained by plotting temperature against the logarithm of K X 10^3. This curve was a straight line from which the velocity constant at 40° was easily obtained.

The Effect of Various Substances upon the Reaction Rate.—The speed of the decomposition of malic acid was determined after various substances had first been dissolved in the sulfuric acid. All of the substances studied were found to inhibit the reaction. The effect of nine solutes was determined at two concentrations and at three different temperatures in order that the effect of the inhibitor upon the temperature coefficient could be observed. The results are summarized in Table II.

TABLE II

EFFECT OF SOLUTES ON THE RATE OF DECOMPOSITION OF MALIC ACID BY SULFURIC ACID

Molality, 0.25

Solute	$K \times 10^3$, 20°	$K \times 10^3$, 30°	$K \times 10^3$, 40°	$\frac{K\times 10^3,\ 30°}{K \times 10^3,\ 20°}$	Crit. increment	$\frac{K\times 10^3,\ 40°}{K \times 10^3,\ 30°}$	Crit. increment
Ammonium sulfate	3.04	13.9	60.4	4.58	26,870	4.33	27,640
Phenol	3.88	19.8	85.7	5.10	28,770	4.33	27,640
p-Cresol	3.71	18.3	78.3	4.95	28,240	4.27	27,380
Coumarin	5.68	23.5	103	4.14	26,090	4.39	27,900
Benzophenone	5.35	22.5	94.0	4.22	25,670	4.18	26,980
Benzoic anhydride	0.336	1.60	8.02	4.76	27,550	5.01	30,400
Ethyl alcohol	6.17	30.4	126	4.93	28,170	4.14	26,800
Benzoic acid	5.46	24.0	101	4.39	26,120	4.22	27,160
Phosphoric acid	5.60	25.7	107	4.58	26,870	4.16	26,890
Acetophenone	5.63	24.8	100	4.41	26,200	4.03	26,900
Triphenylcarbinol		16.6					
m-Nitrophenol		31.3					
o-Toluic acid		21.0					
Crotonic acid		24.9					

Molality, 0.50

Solute	$K \times 10^3$, 20°	$K \times 10^3$, 30°	$K \times 10^3$, 40°	$\frac{K\times 10^3,\ 30°}{K \times 10^3,\ 20°}$	Crit. increment	$\frac{K\times 10^3,\ 40°}{K \times 10^3,\ 30°}$	Crit. increment
Ammonium sulfate	1.33	6.18	27.6	4.64	27,100	4.47	28,240
Phenol	1.64	8.06	38.1	4.91	28,100	4.73	29,310
p-Cresol	1.59	8.10	35.8	5.08	28,670	4.42	25,030
Coumarin	3.20	13.9	61.8	4.34	25,920	4.44	28,120
Benzophenone	3.19	13.3	56.7	4.17	25,220	4.26	27,340
Benzoic anhydride		0.47	2.44			5.19	31,060
Ethyl alcohol	3.77	17.8	72.3	4.72	27,400	4.07	26,470
Benzoic acid	3.25	14.1	59.7	4.35	25,960	4.22	27,160
Phosphoric acid	3.56	16.3	69.9	4.58	26,870	4.29	27,470
Acetophenone	3.39	15.8	63.0	4.66	27,170	3.98	26,050
Triphenylcarbinol		6.30					
Crotonic acid		15.2					

Most inhibitors increase the critical increment slightly although coumarin, benzophenone and benzoic acid have practically no effect at the lower concentration. Benzoic anhydride, which has the greatest effect on the critical increment, is the most pronounced inhibitor. The temperature coefficient of the inhibited reaction decreases, within the limit of experimental error, with increase of temperature. The temperature coefficient of the reaction inhibited by benzoic anhydride at molality 0.25 increases from 4.76 to 5.01. This difference is slightly outside the limit of experimental error. Increase of concentration of the inhibitors from molality 0.25 to 0.50 either slightly increases or does not affect the critical increment. The critical increments were calculated from the Arrhenius equation $d \ln k/dT = E/RT^2$.

The concentrations of the inhibitors were plotted against the logarithms of the velocity constants at each of the temperatures at which the decomposition was studied. The curves so obtained deviated slightly from straight lines. Four typical curves are given in Fig. 1.

Compound Formation between Malic **and** Sulfuric **Acids.**—In discussing the possible mechanism of the decomposition of malic acid by sulfuric acid, Whitford postulated the formation of an unstable molecular compound between the two acids. This addition product was then assumed to decompose into water, carbon monoxide, *a*-pyrone-β'-carboxylic acid, and the original sulfuric acid.

In this investigation evidence for the existence of such a molecular complex was obtained. Knox and Richards[6] showed that it was possible to demonstrate the formation of molecular addition compounds between acids tion by determining the solubility of one acid at a particular temperature in solutions of increasing concentration of the second acid. In cases of compound formation the solubility of the acid at first diminished with increasing concentration of the solvent acid in accordance with the effect of a common ion; but as the concentration of the solvent acid became greater, this influence was offset by the second influence, namely, compound formation between the acids, and the solubility of the solute acid then increased in proportion to the increase of concentration of the solvent acid. In cases where no compounds resulted, the solubility of the first acid continually decreased.

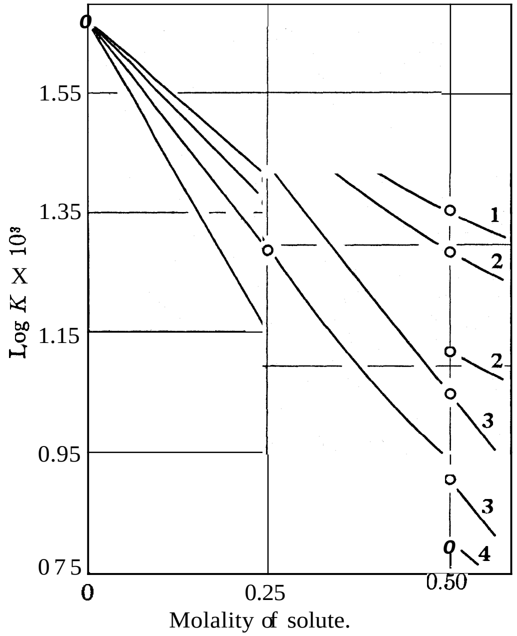

Fig. 1.—Effect of phosphoric acid, 1, coumarin. 2, phenol, 3, and ammonium sulfate, 4, on the reaction rate at 30°.

In accordance with this method the solubility of malic acid was determined in aqueous solutions of sulfuric acid of different concentrations. The concentrations of the sulfuric acid solutions were determined by titration with a standard solution of sodium hydroxide, after which they were saturated with malic acid at about 35° in tightly stoppered glass flasks

[6] Knox and Richards, J. *Chem. Soc.,* 115, 508 (1919).

which were supported in a mechanical agitator. The temperature was decreased to 30° and after equilibrium had been established the solutions were filtered rapidly at 30° through a Gooch crucible. The total acidity of aliquots of the filtered solution was then determined by titration with the standard alkali, and the sulfuric acid present in the solution was determined gravimetrically as barium sulfate. The malic acid content was calculated by difference. In all the titrations phenolphthalein was used as an indicator.

The results are tabulated in Table III, in which the concentrations of both acids are expressed in terms of normality. These data are plotted in Fig. 2 and furnish evidence for the existence of a molecular addition compound between malic and sulfuric acids.

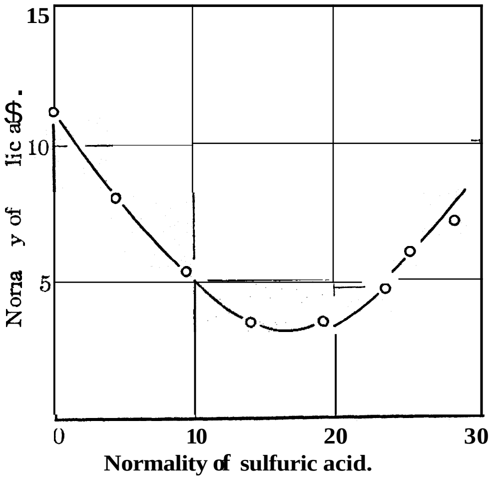

Fig. 2.—Solubility of malic acid in aqueous solutions of sulfuric acid.

Table III

Solubility of Malic Acid in Aqueous Solutions of Sulfuric Acid

Normality of sulfuric acid	Normality of malic acid	Normality of sulfuric acid	Normality of malic acid
0.000	11.21	19.08	3.568
4.212	8.045	23.54	5.005
9.416	5.451	25.26	6.071
14.00	3.568	28.44	7.090

Discussion of Results

Since data pointing to the actual existence of an intermediate compound between sulfuric and malic acids have been obtained, the assumption that the decomposition is affected through the decomposition of such a molecular complex does not appear unlikely. The reaction can be represented as taking place in the following way

$$C_4H_6O_5 + nH_2SO_4 \rightleftharpoons C_4H_6O_5 \cdot nH_2SO_4$$

$$C_4H_6O_5 \cdot nH_2SO_4 \longrightarrow nH_2SO_4 + CO + H_2O + C_3H_4O_3$$

The velocity of the decomposition of the malic acid will then be proportional to the concentration of the molecular complex, which in turn will be dependent upon the effective concentrations of malic and sulfuric acids.

Action of Inhibitors

Whitford postulates that sodium, potassium and silver sulfates, acetic acid and dimethylpyrone inhibit this decomposition because these compounds form molecular complexes with the sulfuric acid, thereby decreasing the active concentration of the latter and preventing it from reacting with the malic acid. In the present investigation all the inhibitors except phosphoric acid and ethyl alcohol have been shown to form molecular addition compounds with sulfuric acid.[7,8,9] McIntosh[10] has isolated an equimolecular addition compound between ethanol and nitric acid, but did not obtain a similar result with sulfuric acid, because at the low temperatures which were employed, the sulfuric acid became extremely viscous. It seems reasonable to suspect that sulfuric acid would show the same tendency toward compound formation with ethanol that nitric acid does.

These facts might be interpreted as substantiating the view that the inhibitors function by combining with the sulfuric acid, as postulated by Whitford, were it not that phosphoric acid inhibits the decomposition even though it has not been shown to form an addition complex with sulfuric acid.

The concentration of sulfuric acid was very much greater than that of the malic acid or the solute. When the molality of the inhibitor was 0.25, each reaction flask contained approximately 500 molecules of sulfuric acid and **12** molecules of inhibitor for every molecule of malic acid. In other words, there were forty molecules of sulfuric acid for every molecule of inhibitor. Granting that inhibition is affected by combination of sulfuric acid with the solute, it is difficult to conceive that such a small concentration would so profoundly affect the reaction velocity. On the other hand, sulfuric acid is a very highly associated liquid. Aston and Ramsay[11] have shown that sulfuric acid which corresponds to the formula $(H_2SO_4)_{12}\cdot H_2O$ has a formula of $(H_2SO_4)_{32}$ at room temperature. If such a large molecule is the active reagent, then the molecular concentration of inhibitor to associated sulfuric acid would be about equal and such an explanation of inhibition could be possible.

The retardation of the reaction rate by a solute can be more satisfactorily explained by assuming that the solute reacts with the malic acid to form a molecular complex, the formation of which decreases the active concentration of the malic acid and so diminishes the concentration of the unstable sulfuric–malic acid complex and hence the decomposition rate.

The reactions may be represented in the following way

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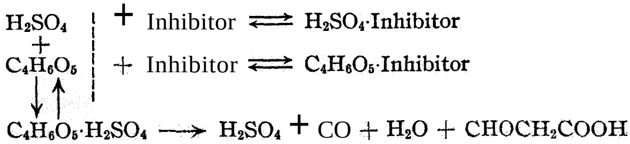
[7] Kendall and Carpenter, THIS JOURNAL, 36, 2498 (1914).

[8] Kendall and Landon, *ibid.*, 42, 2131 (1920).

[9] Dittmar, J. Phys. Chem., 33, 547 (1929).

[10] McIntosh, THIS JOURNAL, 27, 1013 (1905).

[11] Aston and Ramsay, J. *Chem. Soc.*, 65, 167 (1894).



$$\begin{array}{l} H_2SO_4 + \text{Inhibitor} \rightleftharpoons H_2SO_4\cdot\text{Inhibitor} \\ C_4H_6O_5 + \text{Inhibitor} \rightleftharpoons C_4H_6O_5\cdot\text{Inhibitor} \\ H_2SO_4 + C_4H_6O_5 \rightleftharpoons C_4H_6O_5\cdot H_2SO_4 \longrightarrow H_2SO_4 + CO + H_2O + CHOCH_2COOH \end{array}$$

The last mechanism appears more plausible than the first, particularly since the molecular concentration of malic acid is one five-hundredth that of sulfuric acid, for then the effect of removing some of the malic acid by compound formation with the inhibitor would be very much more pronounced on the concentration of the unstable intermediate ($C_4H_6O_5\cdot H_2SO_4$) than would the removal of some of the sulfuric acid.

An attempt to show the existence of some molecular compounds of malic acid with phenol, *p*-cresol, and benzoic anhydride was undertaken by Miss Irene D. Anderson in this Laboratory by making temperature–concentration studies of the two-component systems. In the systems malic acid–phenol and malic acid–p-cresol no reliable data were obtained due to critical solution effects. In the system malic acid–benzoic anhydride decomposition took place, although the curve began to form a definite maximum indicating compound formation.

Since benzoic anhydride forms a molecular compound with malic acid, it should have a marked inhibitory effect upon the reaction rate. It can be seen from Table I that this substance is the most effective negative catalyst.

Kepfer[12] using the solubility method of Knox and Richards has shown that malic and phosphoric acids form an addition compound. This fact will explain the inhibitory power of phosphoric acid, which has not been shown to unite with sulfuric acid.

The lowering of the freezing point of 100% sulfuric acid produced by each inhibitor, at the two concentrations employed in the decomposition experiments, was determined in an attempt to correlate the freezing point depression of a solute with its power as an inhibitor. The results were so irregular that no relationship between these properties was found.

The effect of temperature upon the rate of the inhibited reaction is, as already stated, dependent upon the inhibitor used, although all the inhibitors increase the temperature coefficient. Granting that inhibition is affected through compound formation of the inhibitor with malic or even to some extent sulfuric acid, the effect of temperature upon the reaction rate will be determined by the change in the equilibrium constants in the two following reactions:

$$H_2SO_4 + \text{Inhibitor} \rightleftharpoons H_2SO_4\cdot\text{Inhibitor}$$
$$C_4H_6O_5 + \text{Inhibitor} \rightleftharpoons C_4H_6O_5\cdot\text{Inhibitor}$$

Other than the fact that the first reaction is accompanied, in the case of most inhibitors, with the liberation of heat, the equilibrium constants or

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[12] Walton and Kepfer, *J. Phys. Chem.*, **34**, 543 (1930).

the heats of reaction of the above reactions are not known, and the effect of temperature cannot be accurately predicted. The temperature coefficients of the inhibited reaction at present do not seem to be as much help in the solution of the mechanism of the inhibition as had been anticipated.

Summary

1. The velocity of the decomposition of malic acid by sulfuric acid has been measured in the presence of nine different solutes, all of which retarded the reaction velocity, at two concentrations and three different temperatures.

2. Solubility measurements of malic acid in aqueous sulfuric acid solutions of different concentrations point to the existence of a molecular addition compound between the two, which strengthens the assumption previously expressed by Whitford that the first step in the decomposition of malic acid by sulfuric acid consisted of molecular compound formation.

3. The logarithm of the velocity constant of the inhibited reaction in most cases is not an exact linear function of the concentration of the inhibitor.

4. The critical increment of the reaction is in most cases only slightly increased by the inhibitor.

5. Although all of the inhibitors used, except two, form molecular compounds with one of the reactants of this decomposition—sulfuric acid—the mechanism of the inhibition can be satisfactorily explained, for some solutes, at least, by the formation of addition compounds between the inhibitor and malic acid.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF PRINCETON UNIVERSITY]

THE DETECTION AND ESTIMATION OF SMALL AMOUNTS OF LITHIUM

BY EARLE R. CALEY

RECEIVED APRIL 1, 1930 PUBLISHED JULY 3, 1930

Due to the fact that lithium salts in general are freely soluble in a variety of solvents, few precipitation reactions for lithium are known. Of these none are suitable for the detection and quantitative estimation of very small quantities of this element. It has been found that a relatively sensitive reaction for lithium may be based upon the fact that lithium stearate, in contrast to the stearates of the other alkali metals, is relatively insoluble in certain organic solvents. Unfortunately this reaction cannot be applied in aqueous solutions due to hydrolytic effects, nor can it be used in dilute or concentrated solutions of ethyl alcohol by reason of the solubility of the lithium soap in this solvent. Amyl alcohol was found to be the most convenient medium to use. In the practical qualitative or quantitative application of this reaction, the lithium chloride is extracted from the mixture of alkali chlorides with amyl alcohol and a reagent is used which consists of a solution of ammonium stearate in this alcohol.

Preparation of the Reagent.—The ammonium stearate required for this reagent is conveniently and rapidly prepared by passing dry ammonia gas into a solution of stearic acid in ether according to McMaster's[1] method for preparing the ammonium salts of the higher fatty acids. In practice a 1.6 to 2.0% solution of pure stearic acid in ether should be used and a rapid current of ammonia gas passed in until no further precipitation takes place. During the process, which only takes ten to fifteen minutes with a liter of stearic acid solution, ether should be added from time to time to replace that lost by evaporation. Without this precaution the mixture becomes pasty and difficult to handle. After precipitation is complete, the mixture is poured upon a large glass tray or dish and when the ether has evaporated the material is ready for use. The reagent proper is made by dissolving the powdered ammonium stearate in warm amyl alcohol at the rate of 2 g. for each 100 cc. of the solvent. The amyl alcohol should not be heated above 50° since at higher temperatures the ammonium stearate is more or less rapidly decomposed. On cooling to room temperature the reagent is ready for use. This reagent is a nearly saturated solution of ammonium stearate in amyl alcohol. It should be freshly prepared since it was found that these ammonium stearate solutions evolve ammonia on standing and become useless for reagent purposes in the course of a few days. Amyl alcohol solutions of sodium or potassium stearate were found less satisfactory as reagents due to the lower solubility of these soaps in this solvent.

Experimental Part

General Technique.—The standard solution of lithium chloride used was checked by pipetting out 50-cc. portions and determining the lithium content of these by evaporating with sulfuric acid and weighing as the sulfate. In the experiments where lithium alone was present, measured portions of standard solution were acidified with dilute hydrochloric acid to prevent hydrolysis of the salt, and evaporation to dryness was conducted over a very low burner flame or over the steam-bath. The residual lithium chloride was then dissolved in a measured volume of warm amyl alcohol and, after allowing the solution to cool to room temperature, the reagent was added and the solutions mixed in the usual manner. It was found that agitation had little or no effect in promoting the separation of the lithium stearate, but it was essential to use the solutions at room temperature, due to the appreciable solubility of the soap in warm amyl alcohol. In those experiments where the lithium chloride was mixed with large proportions

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[1] McMaster, **This Journal**, **36**, 1918 (1914).

of sodium and potassium chlorides, the aqueous solution of the salts was evaporated in the same manner and the residue was extracted three or four times with portions of hot amyl alcohol. These extracts were then evaporated to the proper volume and the final solution obtained by pipetting or filtering it off from the small amounts of sodium or potassium chlorides that had separated during the concentration.

Qualitative Experiments.--The first experiments conducted qualitatively were with amounts of lithium approximating **0.001** g. In all of these cases precipitation was almost instantaneous and the precipitate was so large in amount and volume that the mixtures set to a semi-solid mass. The experiments shown in the table indicate the lower limits of sensitivity of the reaction with varying proportions of the amyl alcohol solution of lithium chloride and the reagent.

TABLE I

SMALLEST AMOUNTS OF LITHIUM DETECTABLE WITH AMMONIUM STEARATE REAGENT

Lithium present, g.	Volume of lithium solution, cc.	Volume of reagent, cc.	Precipitation After 5 min.	Precipitation After 60 min.
0.00020	5	5	Slight	Marked
.00010	5	5	Very slight	Marked
.00010	5	10	Slight	Marked
.00010	5	2.5	None	None
.00005	5	10	None	None
.00010	2	5	Marked	Heavy
.00010	2	10	None	Slight
.00005	2	5	Slight	Marked
.000025	2	5	None	None
.00005	1	2.5	Marked	Heavy
.000025	1	2.5	Slight	Marked
.000015	1	2 5	None	None

It was found from these and other experiments that the optimum results were obtained when the volume of reagent was two and one-half times the volume of the amyl alcohol solution. In experiments on the detection of lithium in the presence of sodium and potassium, no difficulty was experienced in extracting **0.0001** g. of lithium from 1 g. of the mixed chlorides and detecting this amount by the method. With careful technique one part of lithium can be detected in admixture with twenty-five thousand parts of the mixed chlorides. Blank experiments made on the sodium and potassium chlorides used gave no evidence of a precipitate. Likewise rubidium and cesium cannot interfere in this method but it is essential that magnesium, the alkaline earths and heavy metals be carefully removed before applying this procedure, since these all interfere.

Quantitative Experiments.—Since the lithium stearate in the above reaction is precipitated in a very finely divided condition, resulting in a suspension the opacity of which increases as the amount of lithium increases, there was suggested a quantitative procedure for the estimation of small amounts of lithium. The method is most conveniently applied by using a series of turbidity standards prepared at the same time that samples are examined. A convenient series is one based upon the use of a 2.0-cc. volume of amyl alcohol solution and 5.0 cc. of reagent, the successive amounts of lithium in such a set being 0.00005, 0.000075, 0.00010, 0.00015, 0.00025 and 0.00040 g. Essential for the success of the process for quantitative purposes is the preparation of the sample and standards under like conditions, more particularly as regards the time and manner of adding the reagent. The latter should be added to the standards and to the samples at the same time and the tubes should be stoppered and shaken in a rack in order to insure the simultaneous mixing of solution and reagent. After shaking, the set of tubes must be allowed to stand for thirty minutes in order to secure complete precipitation. A further shaking of the tubes just before making the comparison promotes the uniformity of the suspensions. With the above series there is no difficulty in estimating the amount of lithium present to within 0.00002 g. when this falls in the lower end of the series or to within 0.00005 g. when it lies in the higher range. The suspensions may also be compared by means of a turbidometer but since samples must be compared with standards that contain approximately the same amount of lithium in order to obtain accurate results, this procedure is only to be recommended as a supplementary method to the comparison with a set of standards. Some typical results obtained in this manner are shown in Table II. The turbidities in these cases were compared by transmitted light in the ordinary plunger type of instrument. Different series of standards may, of course, be prepared, but in dealing with actual samples of rock material, for example, there can be no advantage in having standards ranging below 0.00005 g., due to the practical difficulty of removing minute amounts of interfering calcium and magnesium.

Application to the Usual Quantitative Procedure.—This process can be used to supplement the usual Gooch[2] method for the estimation of lithium in cases where the quantity of that element amounts to a few tenths of a milligram or less, since it is in this region that there is an element of uncertainty with this method due in part to the fact that the applied corrections may exceed the amount of lithium being determined and in part to the natural limitations of the balance. The turbidometric procedure given above enables these small amounts to be determined more accurately than can be done gravimetrically. The method of Gooch can be followed in the usual manner until there is obtained the final amyl alcohol solution containing all the lithium chloride and small amounts of other alkali chlorides. This extract may then be concentrated to a small volume and, after filtering off any separated sodium and potassium chlorides, the lithium

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[2] *F. A.* Gooch, *Proc. Am. Acad. Arts Sci., 22, 177–194* (1886).

TABLE II

ESTIMATION OF SMALL AMOUNTS OF LITHIUM BY THE INSTRUMENTAL COMPARISON OF THE TURBIDITIES PRODUCED BY AMMONIUM STEARATE REAGENT

Lithium present in standards, g.	Observed depths of standards, mm.	Observed depths of samples, mm.	Lithium present in samples, g.	Lithium found in samples, g.	Errors, g.
0.00006	9.3	8.3	0.00009	0.00007	−0.00002
	12.3	10.0	.00009	.00007	− .00002
	10.6	8.5	.00009	.00007	− .00002
.00012	8.9	10.6	.00009	.00010	+ .00001
	11.1	12.5	.00009	.00011	+ .00002
	6.8	7.2	.00009	.00011	+ .00002
.00012	10.8	9.4	.00015	.00014	− .00001
	13.6	9.9	.00015	.00016	+ .00001
	14.0	10.9	.00015	.00015	.00000
.00019	9.6	8.4	.00025	.00022	− .00003
	9.2	7.6	.00025	.00023	− .00002
	9.8	8.3	.00025	.00023	− .00002
.00032	4.6	7.8	.00025	.00019	− .00006
	4.5	7.2	.00025	.00020	− .00005
	7.0	11.4	.00025	.00020	− .00005
.00032	5.2	4.0	.00038	.00042	+ .00004
	3.9	2.8	.00038	.00045	+ .00007
	4.3	3.1	.00038	.00044	+ .00006

may then be precipitated with the proper amount of ammonium stearate reagent and the resulting suspension compared with the series of standards in the manner previously described.

Summary

There has been described a method for the detection and estimation of small amounts of lithium based upon the reaction between ammonium stearate and lithium chloride in amyl alcohol solution.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE ACTIVITY COEFFICIENTS OF IONS IN DILUTE SOLUTION IN ETHYL ALCOHOL-WATER MIXTURES

BY LESTER A. HANSEN AND JOHN WARREN WILLIAMS

RECEIVED APRIL 7, 1930 PUBLISHED JULY 3, 1930

It has been the purpose of a number of recent articles to study the validity of the fundamental equations of the activity theory of Debye and Huckel[1] with respect to the effect of the variation of the dielectric constant of the medium. In spite of definite progress in this direction one must conclude from these articles that the point in question has not as yet been sufficiently investigated. In an earlier article[2] the activity coefficients of several slightly soluble complex cobalt ammine salts of the simpler valence types in pure methyl alcohol were determined and it was possible to show that in these particular solutions the general ideal equations of Debye and Huckel were at least approximately obeyed. For this purpose it was not necessary to use one of the more complete Debye-Hückel equations which take an atomic diameter into account, although by so doing a better agreement with theory might have been accomplished. In the methyl alcohol work it was also evident that difficulties with the simpler equations began to appear with salts of the valence type 3-1, and that the range of applicability of the theory depended upon the solute and saturating salt used. It seemed advisable, therefore, to study the behavior of salts of the 1-1, 1-2 and 3-1 valence types in a solvent whose dielectric constant could be varied at will between 78.8, the dielectric constant of water at 25 and 30°, the approximate dielectric constant of methyl alcohol at the same temperature. Mixtures of water and ethyl alcohol were used for this purpose. The activity coefficients were determined by means of the effect of a solvent salt, sodium chloride, on the solubility of highly insoluble complex cobalt ammine salts of the valence types mentioned above.

Experimental

All solubility measurements were made in a thermostat adjusted to 25". **A** shaft with brass clips attached to hold bottles of 125-cc. capacity was built into the thermostat, in a horizontal position, midway between the top and the bottom of the thermostat can. This shaft could be rotated at a speed such that an excess of salt, when placed in a bottle with the desired solvent, would tumble from one end of the bottle to the other. The saturating salts used were croceo tetranitrodiammino cobaltiate, croceo sulfate and luteo iodate. The solubility of these salts in the various solvent solutions was calculated from analyses for ammonia. A quartz tube five feet long and one inch in diameter, and bent in inverted "U" form, was used as condenser. A 300-cc. pyrex flask was sealed to a pyrex Kjeldahl distilling head which, in turn, was sealed to a pyrex glass tube which

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[1] Debye and Hückel, *Physik.* Z., 24, 185 (1923).

[2] Williams, THIS JOURNAL, 51, 1112 (1929).

fitted snugly over the end of the quartz tube. Gooch rubber tubing was used to make this joint airtight. A side arm one-half inch in diameter, with a ground-glass stopper, was sealed to the flask through which the sample could be admitted. The ammonia passed through the quartz condenser and was absorbed in a known excess of standard hydrochloric acid. Brom cresol purple was used as indicator in the back titration. Two microburets, one of 5-cc. capacity and one of 10-cc. capacity, were used. The burets were calibrated by weighing the quantity of mercury contained in the burets for each large division.

The solvents used were prepared by diluting industrial ethyl alcohol with distilled water. To a part of each solution thus prepared there was added enough sodium chloride to make it 0 1 normal with respect to that salt. Each of these solutions was then diluted with the corresponding solution without the salt in order to give the desired solvent salt concentration.

Chemicals

Cobalt Ammine Salts.—Cobalt ammine salts were obtained from Akatos, the American representative of Kahlbaum. The desired salts were prepared by metathesis with a soluble salt containing the other desired ion. These salts were precipitated from water solutions, washed until freed of electrolytes and finally washed with alcohol and dried.

Sodium Chloride.—The sodium chloride used was obtained from J. T. Baker Chemical Company and was of the "purified" quality.

Sodium Hydroxide.—The sodium hydroxide was obtained from the J. T. Baker Chemical Company. A 20% solution of this reagent was used to decompose the cobalt ammine salts.

Standard Acid.—Approximately 0.02 normal solution of hydrochloric acid was prepared. The acid was standardized, using sodium carbonate prepared by the U. S. Bureau of Standards.

Standard Base.—Approximately a 0.02 normal solution of sodium hydroxide was prepared and standardized with benzoic acid obtained from the U. S. Bureau of Standards.

Results

The solubility relations of the three difficultly soluble salts in the various solvents are presented in Tables I to X, inclusive. With the exception of the data given in Table I they have been determined by us and are average values of the number of determinations indicated in the second column of the tables. In addition the values of the logarithm of the solubility, log S/S_0, obtained directly from the analytical data have been plotted against the square roots of the ionic strengths. The concentrations in the

TABLE I[a]

SOLUBILITY RELATIONSHIPS OF THE 1-1 TYPE SALT CROCEO-TETRANITRO-DIAMMINO COBALTIATE IN WATER AT 20°

Concn. (NaCl) solvent salt	Soly. X 10^4	μ	$\sqrt{\mu}$	Log S/S_0
0 0000	3 70	0 000370	0.0192	0.0000
.0010	3 78	.001378	.0372	,0090
.0020	3.83	.002383	.0480	.0149

[a] These data are taken from Bronsted and La Mer, THIS JOURNAL, 46, 572 (1924).

TABLE II

SOLUBILITY RELATIONSHIPS OF THE 1–1 TYPE SALT CROCEO-TETRANITRO-DIAMMINO COBALTIATE

In 20 **mole** % EtOH–80 **mole** % *water* **at** 25°

Concn. (NaCl) solvent salt	No. of detns.	Soly. $\times 10^4$	μ	$\sqrt{\mu}$	Log S/S_0
0 0000	8	2.420	0 0002420	0.01556	0 0000
.0010	4	2.520	,0012520	,03538	0176
.0020	4	2.587	.0022587	,04753	0290
0030	4	2.634	,0032620	,05711	.0368
,0040	4	2.687	,0042687	,06534	.0455
.0050	4	2.720	0052720	07264	.0508
0075	3	2.753	0077753	08818	0560
.0100	4	2.787	,0102787	,10140	,0613

TABLE III

SOLUBILITY RELATIONSHIPS OF THE 1–1 TYPE SALT CROCEO-TETRANITRO-DIAMMINO COBALTIATE

In 40 **mole** % EtOH–80 **mole** % *water* **at** 25°

Concn. (NaCl) solvent salt	No of detns.	Soly. $\times 10^4$	μ	$\sqrt{\mu}$	Log S/S_0
0.00000	6	1.120	0 000112	0 01058	0 0000
.00100	4	1 200	.001120	,03347	0299
.00250	4	1.267	002626	05123	.0534
.00375	4	1 306	003880	06230	.0669
.00500	4	1 353	,005135	07166	.0821
.00750	4	1 420	,007642	08741	,1031
.01000	3	1 466	,010146	,10075	1169

TABLE IV

SOLUBILITY RELATIONSHIPS OF THE 1–1 TYPE SALT CROCEO-TETRANITRO-DIAMMINO COBALTIATE

In 60 **mole** % EtOH–40 **mole** % *water at* 25°

Concn. (NaCl) solvent salt	No of detns.	Soly. $\times 10^5$	μ	$\sqrt{\mu}$	Log S/S_0
0.0000	6	3 667	0 00003667	0 006055	0 0000
,0010	4	4 000	00104000	032250	.0378
,0030	4	4 533	00304533	055190	0922
.0050	3	4 867	00504867	071050	,1230
.0075	3	5 133	,00755133	.086900	.1461
.0100	3	5 333	01005333	.100300	.1627

TABLE V

SOLUBILITY RELATIONSHIPS OF THE 1–2 TYPE SALT CROCEO SULFATE IN WATER AT 25°

Concn. (NaCl) solvent salt	No. of detns.	Soly $\times 10^3$	μ	$\sqrt{\mu}$	Log S/S_0
0,0000	14	2 447	0 007341	0 08568	0 0000
.0010	4	2 489	,008467	,09202	.0074
.0020	4	2.524	.009572	,09784	.0135
.0030	3	2 564	.010683	.10330	,0198
.0040	3	2.584	011750	.10820	.0240
.0050	4	2 614	,012842	,11330	.0287
.0075	3	2.684	,015552	,12470	.0402
.0100	3	2.754	.018262	.13510	.0513

TABLE VI

SOLUBILITY RELATIONSHIPS OF THE 1–2 TYPE SALT CROCEO SULFATE In 20 mole % EtOH–80 mole % water at 25°

Concn. (NaCl) solvent salt	No of detns.	Soly X 10^4	μ	$\sqrt{\mu}$	Log S/S_0
0 0000	10	1 115	0 000334	0 01829	0 0000
.0010	4	1 21	,001363	,03692	.0355
.0020	4	1 26	,002378	,04877	.0532
0040	4	1 34	,004402	,06635	.0798
0050	4	1 39	.005417	.07360	.0957
0075	4	1 45	,007935	.08908	.1141
.0100	3	1.52	,010456	.10220	.1346

TABLE VII

SOLUBILITY RELATIONSHIPS OF THE 1–2 TYPE SALT CROCEO SULFATE In 40 mole % EtOH–60 mole % water at 25°

Concn (NaCl) solvent salt	No of detns.	Soly. X 10^5	μ	$\sqrt{\mu}$	Log S/S_0
0 0000	16	2 00	0 0000600	0.00775	0.0000
0010	8	2 35	.001070	.03272	.0700
.0025	3	2.65	,002577	.05076	.1222
0050	9	3 00	,005087	,07130	.1761
0075	4	3 25	,007597	,08716	.2109
.0100	3	3 45	.0101035	.10050	.2368

TABLE VIII

SOLUBILITY RELATIONSHIPS OF THE 3–1 TYPE SALT LUTEO IODATE IN WATER AT 25°

Concn (NaCl) solvent salt	No of detns.	Soly. × 10^3	μ	$\sqrt{\mu}$	Log S/S_0
0 0000	10	5 270	0 03162	0.1778	0.0000
.0010	6	5 362	03250	.1803	.0075
.0020	5	5.384	.03428	.1852	.0093
,0030	4	5.478	.03587	.1896	.0178
.0040	6	5.557	,03734	.1932	.0230
0050	6	5.698	,03820	.1980	.0339
.0100	4	5.846	.04500	.2121	.0451

TABLE IX

SOLUBILITY RELATIONSHIPS OF THE 3–1 TYPE SALT LUTEO IODATE In 20 mole % EtOH–80 mole % water at 25°

Concn. (NaCl) solvent salt	No. of detns.	Soly. X 10^4	μ	$\sqrt{\mu}$	Log S/S_0
0.0000	8	1.553	0 000932	0.03032	0 0000
.0010	7	1.800	.002080	,04561	0641
.0020	5	1.987	.003192	.05650	.1070
.0025	6	2 120	,003770	.06140	.1351
.0050	7	2.400	,006430	08020	,1890
.0075	4	2.687	.009110	.09545	2381
.0100	6	2.820	.011690	.10800	.2591

table are moles per liter. These plots are given in Figs. 1 to **3,** in which the numbers attached to each line give the number of the table from which the data were taken for the graph.

TABLE X

SOLUBILITY RELATIONS OF THE 3-1 TYPE SALT LUTEO IODATE

In 40 mole % EtOH-60 mole % water at 25°

Concn (NaCl) solvent salt	No of detns.	Soly. X 10^5	μ	$\sqrt{\mu}$	Log S/S_0
0 0000	10	2 002	0 000120	0 01096	0 0000
0010	6	2 800	001168	03418	,1458
.0025	8	3.500	002710	,05206	.2427
.0050	10	4.689	,005280	07268	3707
.0075	6	A 300	007878	.08876	,4979
.0100	8	7.787	,010467	.10230	,5901

Discussion

The results of the calculations of Debye and Huckel for the activity coefficient of a salt in a dilute solution are given by the equation

$$-\ln f_s = \frac{\Sigma\nu_i z_i^2}{\Sigma\nu_i} \cdot \frac{\epsilon^2}{DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} \Sigma N_i z_i^2} = \alpha z_1 z_2 \sqrt{\mu} \tag{1}$$

The significance of the various factors in the equation is now well known. Since the experiments were made at a single temperature, the value of α will depend upon the dielectric constant of the solvent and certain universal constants. For our purpose it may be said that the negative of the loga-

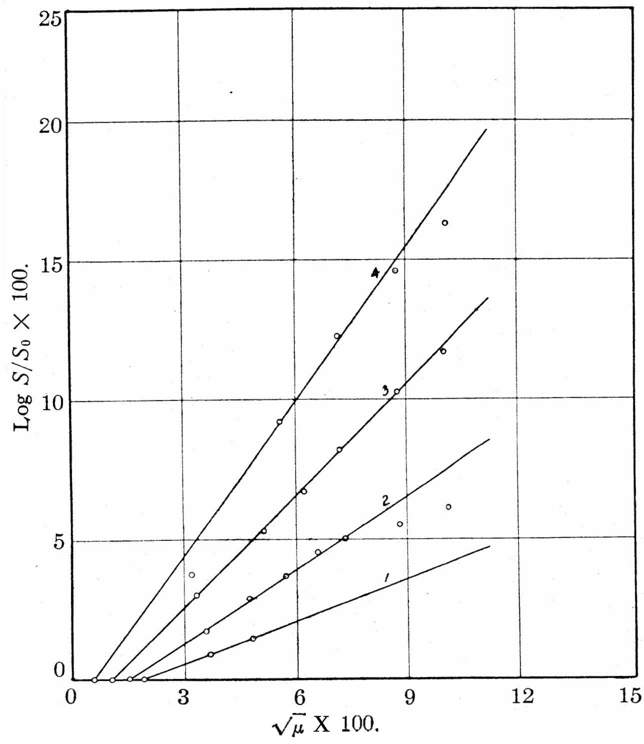

Fig. 1.

rithm of the activity coefficient of the salt varies inversely as the dielectric constant, raised to the three-halves power. The dielectric constants of the various solvents used are given in Table XI. The comparison of the limiting slopes obtained for the different systems with those predicted on the basis of the simple theory expressed by the equation given above is given in Tables XII to XIV, inclusive. The calculations represented in these tables did not take an ionic diameter into account. One must conclude from Tables XII and XIII that the validity of the simple limiting law is completely established for the saturating salts of valence types 1–1 and 1–2 even in solvents whose dielectric constants are as low as one-half that of water. This result is of interest because a similar conclusion

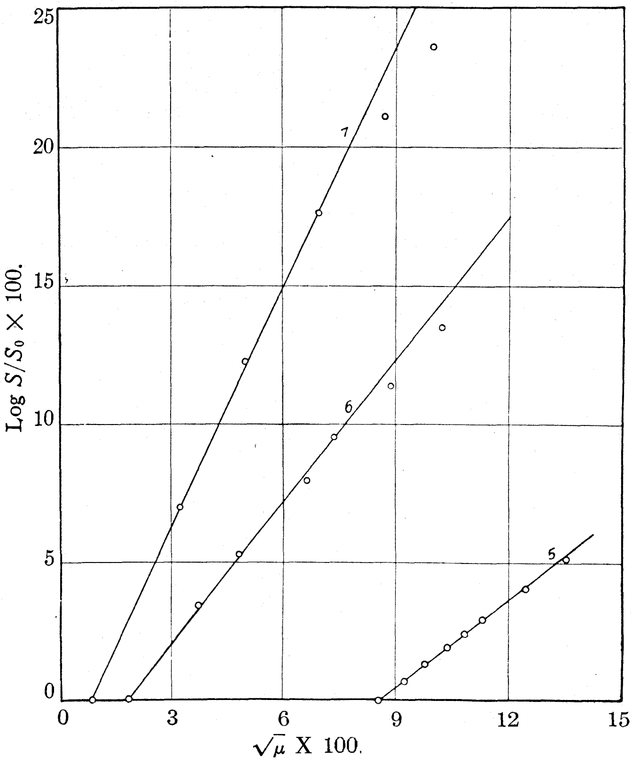

Fig. 2.

TABLE XI

DIELECTRIC CONSTANTS OF ALCOHOL–WATER MIXTURES[a]

Mole % alcohol...............	60	40	20	00
Dielectric constants............	33 8	41 4	54.0	78.8

[a] These figures have been obtained by interpolation of data used by Scatchard, THIS JOURNAL, 47,2102 (192.5).

was drawn in the preceding paper of the series[2] for salts of the same valence types dissolved in pure methyl alcohol.

TABLE XII

1–1 TYPE SALT CROCEO-TETRANITRO DIAMMINO COBALTIATE

Solvent	Slope (obs)	Slope (calcd)
Water . .	0 50	0 504
20 Mole % EtOH–80 mole % water	0 89	0 888
40 Mole % EtOH–60 mole % water	1 31	1 324
60 Mole % EtOH–40 mole % water	1 90	1 790

TABLE XIII

1–2 TYPE SALT CROCEO SULFATE

Solvent	Slope (obs)	Slope (calcd)
Water	1 10	1 08
20 Mole % EtOH–80 mole % water	1 74	1 76
40 Mole % EtOH–60 mole % water	2 74	2 65

TABLE XIV

3–1 TYPE SALT LUTEO IODATE

Solvent	Slope (obs.)	Slope (calcd.)
Water..............................	1.52	1.51
20 Mole % EtOH–80 mole % water.....	4.0	2.65
40 Mole % EtOH–60 mole % water.....	6.1	3.98

However, it is evident from Table XIV that the simple limiting law is obeyed only in pure water for the salt of valence type 3–1. When the dielectric constant of the medium has been reduced to 54, the observed slope is considerably higher than the theoretical, a fact which is also true with solvents having even lower dielectric constants. Unpublished data show exactly the same phenomenon for luteo bromide, a salt of valence type 1–3, in methyl alcohol solution. However, one must be careful not to draw the conclusion that these data are not at all in agreement with the interionic attraction theory. As a matter of fact, from the nature of the forces acting, the qualitative statement may be made that the deviations are in the right direction and of a proper order of magnitude.

We do not feel that either data or theory are at present sufficient to account quantitatively for these deviations, since the salt is of a highly unsymmetrical valence type. Nevertheless, it seems worth while to mention certain possibilities in this connection. If, instead of considering the ions as point charges, their diameters are taken into consideration, Equation 1 may be modified as follows

$$-\ln f_s = \alpha z_1 z_2 \sqrt{\mu} \cdot \frac{1}{1 + a\kappa} \qquad (2)$$

where a is the "effective diameter" of the ions and

$$\kappa = \sqrt{\frac{4\pi\epsilon^2}{DkT} \Sigma n_i z_i^2}$$

This equation, either used directly, or when expanded in ascending powers of μ, has achieved certain success in extending the range in which the equation may be applied with success. It is, however, of little assistance in the present difficulty because if one attempts to find an ionic diameter which will be consistent with the experimental data at the different concentrations, the values obtained are not constant and are of questionable physical significance.

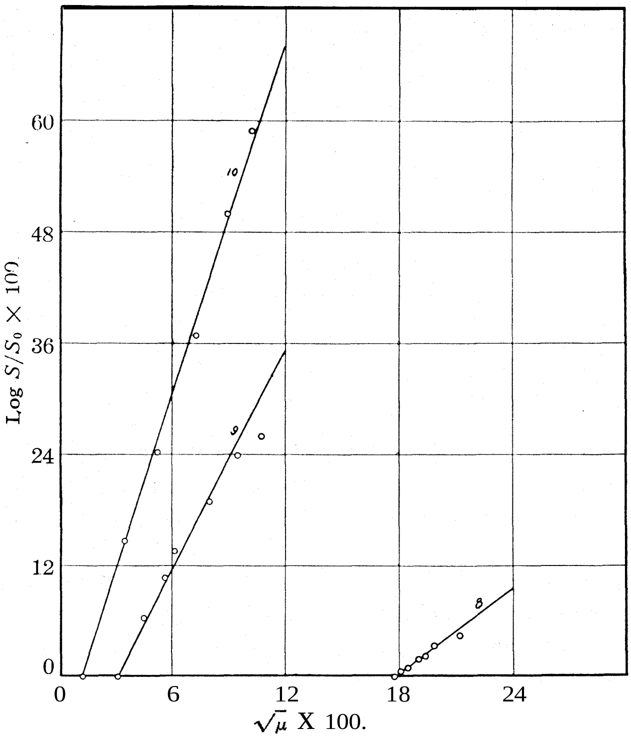

Fig. 3.

A second possibility is presented in the consideration of the influence of the so-called "higher terms"[3] which have been willfully neglected in the interest of simplicity in the original article of Debye and Hückel, but which have more recently been taken into account by Müller[4] and by Gronwall, La Mer and Sandved.[5] It has appeared possible in this way to avoid the difficulty of improbable values for the ionic diameters in the case of symmetrical valence type salts (that is, uni-univalent, bi-bivalent, etc.), but as far as the present authors are aware the calculations for unsymmetrical valence type salts have not as yet been made.

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[3] See Debye and Huckel, *Physik. Z.*, 24, 190 (1923).

[4] Muller, ibid., 28, 324 (1927); 29, 78 (1928).

[5] Gronwall, La Mer and Sandved, *ibid.*, 29, 358 (1928).

Bjerrum[6] has noted that the deviations from the simple Debye–Hückel relations appear in the direction that would be expected if some undissociated molecules were present. Arguing that the sin *hyp* ($\epsilon\psi/kT$) term which has been expanded by others[k5] cannot be evaluated exactly, he has proceeded to an approximate solution of the difficulty by assuming that a small fraction of the total number of oppositely charged ions are "paired" or "associated." There has been introduced a certain degree of arbitrariness in assigning the term "associated to a pair of oppositely charged ions whose centers approach more closely than a certain empirical distance; nevertheless the point of view has much to recommend it for use in the solvents of lower dielectric constant.

It may well be, however, that our difficulty cannot be solved in a quantitative way by the use of one of these extensions of the Debye and Hiickel equations. It will be recalled that in the interionic attraction theory the thickness of the ionic atmosphere of mean charge surrounding each ion is proportional to the square root of the concentration, ***provided*** the principal forces between the ions are the ordinary Coulomb forces. Therefore, if salts of highly unsymmetrical valence types are dissolved in these solvents of lower dielectric constants, their activities may fail to be given by the simple equation or any of the present extensions because the principal forces between the ions can no longer be expressed by Coulomb's law. This possibility is now being subjected to further study.

Summary

1. The activity coefficients of slightly soluble complex cobalt ammine salts of valence types 1–1, 1–2 and 3–1 have been determined in various mixtures of ethyl alcohol and water. These data have been used to test the validity of the simple Debye and Huckel equations.

2. The general ideal equations of the interionic attraction theory are obeyed in those solvents having dielectric constants even as low as one-half that of water for saturating salts of the valence types 1–1 and 1–2, provided the solutions are sufficiently dilute.

3. A marked deviation from the simple limiting law occurs in the case of the 3–1 type salt studied when the dielectric constant of the solvent is reduced below that of water by an appreciable amount. The deviation has been qualitatively but not quantitatively accounted for.

MADISON, WISCONSIN

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[6] Bjerrum, *Det. **Kgl.** Danske **Videnskab Selskab,** Math.-fys. **Medd.,** VII, 9 (1926).* (in German).

[CONTRIBUTION FROM THE DEPARTMENT OF MEDICAL RESEARCH, DETROIT COLLEGE OF MEDICINE AND SURGERY]

THE STARCH–IODIDE REACTION: STABILITY AND PROPORTIONALITY OF COLOR PRODUCED BY SMALL AMOUNTS OF IODINE

BY R. G. TURNER

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Numerous investigators have discouraged the use of the starch–iodide reaction as a basis for the colorimetric estimation of small amounts of iodine. McClendon[1] objects to the titration method because of the ease of oxidation of potassium iodide. Nichols[2] showed the retarding effect of various salts on the sensitivity of the starch reagent. Von Fellenberg[3] attempted to use the starch–iodide reaction for the colorimetric estimation of small amounts of iodine He states that in salt solutions it is of little value in quantitative iodine determinations, since the intensity is not always proportional to the iodine content. Treadwell and Hall[4] as cited by Nichols have shown that starch paste requires the presence of an alkali iodide to prevent the dissociation of the blue iodide–starch color. Nichols[2] fulfilled the requirements for a stabilized starch solution. He eliminated the use of salt or chloroform as a preservative and in its place used salicylic acid. This reagent is sensitive, stable and with iodine produces a true blue color.

Failing to obtain satisfactory results in estimating minute amounts of iodine by the method of von Fellenberg[5] and Leitch and Henderson,[6] a study was made of the starch–iodide reaction in regard to the proportion of iodine present and the intensity of color produced. This investigation was carried out with minute amounts of iodine ranging from 0.0005 to 0.005 mg. These small amounts were chosen as the purpose in mind was to find a suitable method for the quantitative estimation of iodine in small quantities of blood.

Comparative tests were made on potassium iodide test solutions to determine the relative proportion of iodine present to the intensity of color produced, the stability of the color and effect of temperature on the production of the color.

Experimental

The study was made with aqueous solutions of potassium iodide. A standard solution containing 0.001 mg. of iodine in the form of potassium iodide was prepared in the following manner.

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[1] J. F. McClendon, THIS JOURNAL, **50**, 1093 (1928).

[2] M. Starr Nichols, *Ind. Eng. Chem., Analytical Ed.*, **1**, 215 (1929).

[3] T. von Fellenberg, *Ergebnisse der Physiol.*, **25**, 176 (1926).

[4] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1914, Vol. I, p. 299.

[5] T. von Fellenberg, *Biochem. Z.*, **139**, 371 (1923); **152**, 116 (1924).

[6] Isabella Leitch and J. M. Henderson, *Biochem, J.*, **20**, 1003 (1926).

1.3081 g. of recrystallized potassium iodide is weighed out and transferred to a 100-cc. volumetric flask containing 50 cc. of purified water. After dissolving, dilute to 100 cc. (0.1 cc. of this solution is equivalent to 1 mg. of iodine). A weak solution is made by adding 0.1 cc. of the above solution to a liter volumetric flask and diluting to the mark. (1 cc. of this solution is equivalent to 0.001 mg. of iodine.) The accuracy of the weak solution may be checked by titrating 200 cc. with a 0.005 *N* thiosulfate solution which has been previously standardized against a 0.005 *N* solution of potassium iodate.

Take 200 cc. of potassium iodide standard, acidify with 2 N sulfuric acid and add saturated bromine water until the solution is colored orange. Boil off excess bromine and cool. Add a few salicylic acid crystals, 2 cc. of starch solution and an excess of potassium iodide crystals. Titrate with 0.005 *N* thiosulfate.

Test solutions were prepared from the standard solution by delivery from a buret graduated to 0.1 cc.

The technique used for developing the color is based on the method of Leitch and Henderson,[6] which involves the oxidation of hydriodic acid to iodic acid and the liberation of the iodine by addition of an excess of potassium iodide. Kendall and Richardson[7] have shown that this reaction quantitatively produces six times the amount of iodine originally present.

$$HIO_3 + 5HI = 3H_2O + 3I_2$$

The oxidation and production of the color for study are carried out in a 15-cc. pyrex test-tube graduated at 1 cc. The test solution is diluted to 2 cc. and acidified with two drops of 2 N sulfuric acid. Three drops of freshly prepared saturated bromine water are added. After one-half minute the excess bromine is boiled off over a low micro burner flame and the volume of liquid in the test-tube is evaporated to one-half cc. This must be done cautiously. By holding the tube in a slanting position and continually rotating, no spitting or loss of liquid takes place. While still hot, add 1 drop of a 1% alcoholic salicylic acid solution and place the tube in a beaker of cold water. A standard solution of potassium iodide containing 0.001 mg. of iodine is prepared in a like manner. When cooled to room temperature, add to each tube five drops of starch solution (prepared according to Nichols)[8] and three drops of 1% potassium iodide solution. Dilute with iodine-free water to the 1-cc. mark. A blue color will form immediately. If necessary, the test solution is diluted to match the standard. The colors are compared in a micro-colorimeter. The standard is set at 20 mm. The iodine present in the test solution is calculated from the observed reading by the formula

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[7] E. C. Kendall and F. S. Richardson, J. *Biol. Chem.*, 43, 149 (1920).

[8] One-half g of soluble potato starch is added to 2.5 cc. of cold water and mixed to form a thin paste. Pour it gradually with constant stirring into 200 cc. of water. Boil for fifteen minutes, stirring continually. Allow to cool and add 0.25 g. of salicylic acid. Stir until the preservative is dissolved. Fresh starch solution should be prepared every two weeks. If a good grade of starch is used the solution will be clear and filtration unnecessary. Poor grades of starch may produce cloudy solutions and filtrates of a faint pink color.

$$\frac{\text{Reading of standard}}{\text{Reading of test solution}} \times \frac{0.006}{6} \times \frac{\text{dilution of test solution}}{\text{dilution of standard}} = \text{mg. of iodine present}$$

For example, with a reading of 15-mm. dilution of test solution 2 cc. and standard set at **20** mm., the formula is applied as follows

$$\frac{20}{15} \times \frac{0.006}{6} \times \frac{2}{1} = 0.0026 \text{ mg. of iodine}$$

All glassware used must be cleaned with cleaning solution. Traces of organic matter or alkali soaps interfere with the reaction. Iodine-free water is obtained by redistilling distilled water from potassium hydroxide.

The experimental results are shown in the tables.

Table I

Accuracy of Starch–Iodide Colorimetric Method

Reading of standard 0.001 mg. iodine, mm.	Test KI solution iodine, mg.	Obs. reading of test solution, mm.	Iodine found, mg.	Calcd. reading, mm.	Iodine calcd., mg.
20	0.0005	35.4	0.00056	40.0	0.0005
20	.0006	32.7	.00061	33.3	.0006
20	.0007	29.0	.00068	28.5	.0007
20	.0008	24.6	.00081	25.0	.0008
20	.0009	21.8	.00091	22.2	.0009
20	.0010	19.8	.00101	20.0	.0010
20	.0011	18.4	.00108	18.1	.0011
20	.0012	17.0	.00117	16.6	.0012
20	.0013	14.6	.00139	15.3	.0013
20	.0014	13.8	.00144	14.2	.0014
20	.0015	12.9	.00155	13.3	.0015
20	.0016	12.4	.00161	12.5	.0016
20	.0017	11.2	.00178	11.7	.0017
20	.0018	11.0	.00181	11.1	.0018
20	.0019	10.2	.00196	10.5	.0019
20	.0020	10.0	.00200	10.0	.0020

Table II

Comparative Readings on Diluted Test Solutions. Standard (0.001 Mg. of Iodine) Set at 20 Mm.

Test solution, mg. of iodine	Colorimeter reading, mm.	Dilution of test solution, cc.	Iodine found, mg.
0.001	20.2	1	0.00099
.001	21.0	1	.00095
.001	20.0	1	.00100
.002	10.2	1	.00196
.002	19.4	2	.00206
.002	21.0	2	.00190
.003	13.0	2	.00308
.003	20.4	3	.00294
.004	10.5	2	.00380
.004	21.2	4	.00376
.005	21.0	4	.00475

TABLE III

STABILITY OF COLOR PRODUCED BY THIS METHOD. STANDARD (0.001 MG. OF IODINE) SET AT 20 MM.

Test solution (γ) = 0.001 mg	Dilution, cc	Readings on colorimeter scale 5 min., mm	15 min., mm	30 min., mm	60 min., mm.	16 hrs., mm
KI = 1γ Iodine	1	20.9	21.0	20.4	21.1	19.6
KI = 2γ Iodine	1	10.4	10.3	10.5	10.4	13.0
KI = 3γ Iodine	2	13.8	13.5	13.8	13.3	16.7
KI = 1γ Iodine	1	19.9	20.1	20.3	20.0	18.1
KI = 6γ Iodine	3	10.4	10.0	10.6	10.6	9.3

Discussion

From the observations given it is evident that minute amounts of iodine ranging from 0.0005 to 0.005 mg. produce, under the conditions given, a true blue color which is proportional in intensity to the amount of iodine present. The color produced can easily and clearly be matched in a microcolorimeter with an accuracy of 0.0001 mg. in the colorimetric reading.

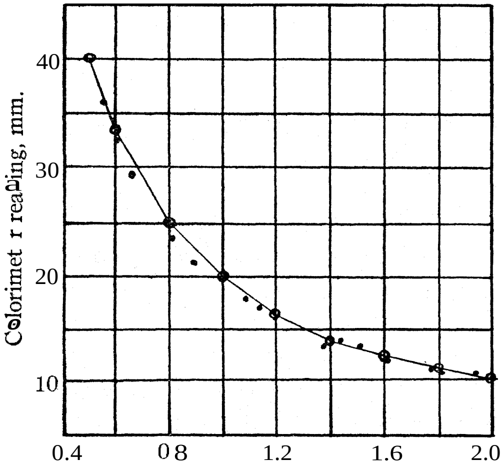
The observations in Table I show the relative proportionality of iodine present to the amount of color produced. The test solutions were prepared from the standard potassium iodide solution ranging in iodine content from 0.0005 to 0.002 mg. The iodine found by colorimetric reading did not vary in any case given more than 0.0001 mg. from the actual amount of iodine present. Amounts below 0.0005 mg. cannot be compared against a 0.001 mg. standard unless the standard is diluted to 2 cc. Such small amounts may have a slight pinkish color which interferes with the sharpness of the reading, though approximate estimations can be made.

Table II gives the comparative readings and estimations of iodine on diluted test solutions. The error in the colorimetric estimation reaches 0.0002 mg. in solutions containing over 0.003 mg. of iodine. The same error made in a colorimetric reading on a solution diluted as made on a solution of the same volume as the standard results in a greater error of the calculated value. If the test solution is diluted to 2 cc., then the final error due to colorimetric reading will be twice as great as the same error made if standard and unknown are of equal volume.

The chromogenic color remains stable for one hour or more when compared against a standard prepared at the same time as the test solution (Table III). Readings at a period of sixteen hours after the colors were formed showed a slight increase in the amount of color present. This increase appears to be greater the higher the original iodine content. This may be due to the partial formation of a colloidal suspension or to oxidation of the excess potassium iodide by oxygen of the air. Comparison of the stability with a new standard at each interval of time showed no change in twenty minutes, after which readings became slightly higher (not recorded in table). A slow oxidation of the excess potassium iodide probably takes place but under like conditions this change is proportional for one hour at least, which is sufficient time for colorimetric reading.

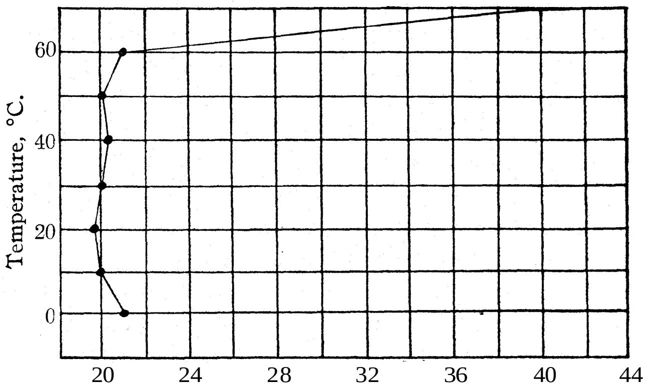
Figure 1 shows the calculated colorimetric curve as compared against the observed findings in Table I.

Figure 2 shows the effect of temperature on color formation. The color production was carried out at temperatures ranging from 0 to 90°. Readings were made while the solutions were at these temperatures. Even at 60° the colorimetric reading varied only 1 mm. At 70° only a slight color was produced, while above that no color was formed. After cooling for one hour, the maximum color developed' in those which were negative at the high temperature.



γ Iodine (1γ = 0.001 mg).
○, Calculated; ●, observed.
Fig 1.—Color curve.

The sensitiveness of this reaction and the stability of the color produced is accomplished no doubt because of the small amounts of iodine estimated and the fact that no interfering salts are present.



Colorimeter reading, mm.
Fig. 2.—Temperature curve.

It is believed that in the estimation of so small quantities of iodine, titration with most extreme cautiousness cannot perform as accurate a quantitative iodine determination as a colorimetric comparison in a microcolorimeter against a 0.001 mg. standard.

Investigation is under way to determine whether amounts of iodine greater than **0.005** mg. may be determined colorimetrically by use of the starch–iodide reaction.

Summary

1. The color produced by starch and iodine in the absence of other salts may be used as a colorimetric measurement of the iodine present in amounts ranging from **0.0005** to **0.005** mg. with an accuracy of **0.0001** mg. in the colorimetric reading.

2. The color produced is proportional to the amount of iodine present.

3. The chromogenic substance is stable for at least one hour when compared against a standard made at the same time.

4. Temperature has no effect on the intensity of the color produced up to 70°, after which the color produced is less.

DETROIT, MICHIGAN

[CONTRIBUTION PROM THE CHEMICAL DIVISION OF THE MEDICAL CLINIC OF THE JOHNS HOPKINS UNIVERSITY]

OXIDATION–REDUCTION POTENTIALS AT CARBON AND TUNGSTEN ELECTRODES

BY LOUIS B. FLEXNER AND E. S. GUZMAN BARRON

RECEIVED APRIL 10, 1930 PUBLISHED JULY 3, 1930

It has been shown[1] that the potentials of cysteine solutions obtained at mercury electrodes are related to mercury-thiol compounds and doubt was cast upon the significance of the potentials obtained at platinum and gold electrodes. It was thought probable that further light would come from investigation of the behavior of cysteine at other electrodes. Of several of these studied, carbon and tungsten appear most promising. This note concerns the behavior of carbon and tungsten electrodes with simple oxidation–reduction systems, the understanding of which must precede investigations on the more complex cysteine systems. Pure graphite was obtained from the Acheson Graphite Company. Tungsten wire came through the courtesy of the General Electrical Company.

The behavior of graphite and tungsten was first studied in two well-poised oxidation–reduction systems of fairly positive E_0. Quinhydrone was first chosen, measurements being made in the presence of air. Table I shows excellent agreements between graphite and gold-plated platinum electrodes in quinhydrone systems in Michaelis' standard acetate buffer, Sørensen's phosphate mixtures, and $N/10$ hydrochloric acid. Purity of carbon is here unimportant, the rods of a carbon arc lamp or the core of a "lead" pencil giving identical results. Tungsten on the other hand gives entirely discrepant values.

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[1] **Barron, Flexner and Michaelis, J.** ***Biol. Chem.*****, 81, 743 (1929).**

TABLE I

THE POTENTIALS OF QUINHYDRONE AT GRAPHITE AND GOLD-PLATED PLATINUM ELECTRODES (AGAINST SATURATED CALOMEL ELECTRODE, TEMPERATURE 20°)

Electrode	E m f. in volts	Substance
C	+0 38835	$N/10$ HCl
Au–Pt	+ .3886	
C	+ .18015	Michaelis' standard acetate
Au–Pt	+ ,18025	
C	+ ,04805	Sørensen's phosphate mixture
Au–Pt	+ ,04800	

Reference to Table II gives results typical for a ferro–ferricyanide system in the presence of purified nitrogen. Throughout the titration, the potential at carbon is 1 to 1.5 millivolts more negative than at platinum and gold, whereas tungsten gives values 5 to 10 millivolts more negative than the noble metals. The potential is established with the same rapidity at all these electrodes.

TABLE II

THE POTENTIAL OF A FERRO–FERRICYANIDE SYSTEM AT GOLD-PLATED PLATINUM, PLATINUM, GRAPHITE AND TUNGSTEN ELECTRODES

T, 30°. $M/1000$ $K_4Fe(CN)_6$ in $M/1$ KCl titrated with $K_3Fe(CN)_6$ ($M/10$ in $M/1$ KCl)
E in volts referred to the normal hydrogen electrode

Au	Pt	C	W	$M/10$ $K_3Fe(CN)_6$ added
+0.4117	+0 4114	+0.4037	+0.3684	0.04
.4400	.4398	.4367	.4277	.14
.4524	.4523	.4503	.4397	.21
.4560	.4560	.4540	.4457	.27
.4643	.4641	.4626	.4544	.39
.4730	.4729	.4716	.4642	.51
.4777	.4776	.4763	.4694	.64
.4830	.4830	.4816	.4751	.78
.4891	.4891	.4881	.4820	1.02
.4947	.4947	.4937	.4880	1.23
.4985	.4985	.4975	.4921	1.43
.5043	.5043	.5033	.4982	1.74
.5066	.5066	.5056	.5005	1.84
.5083	.5083	.5075	.5031	2.00
.5112	.5113	,5104	.5056	2.18

The behavior of graphite and tungsten electrodes was then studied in oxidation–reduction systems nearer the cysteine range, and for this purpose indigo disulfonate and methylene blue were used. The results with indigo disulfonate alone will be discussed here—they can be accepted as completely typical of methylene blue. Reference to Table III shows that there is excellent agreement between graphite, gold and platinum electrodes throughout the titration range of the dye. Until the dyestuff system is about 2% reduced, it is necessary to wait approximately one-half hour for the final values at graphite, Thereafter this electrode gives the same sharp, rapidly established potentials as the platinum and gold. Failure to wait for final values at graphite in the early stages of dye reduction produces a discrepancy between its potential and that of platinum which persists until there is approximately 20% dye reduction. This last result is not to be explained by presence of oxygen in the carbon (carbon adsorbs 80% more oxygen than nitrogen), for heating the carbon rod at 400° in a current of purified nitrogen was without benefit. It is noteworthy that graphite rods in these last experiments are easily "poisoned," and often give reliable results in but a single experiment. Crude carbon is unusable.

TABLE III

TITRATION OF INDIGO DISULFONATE WITH $Na_2S_2O_4$

Concentration of dye, *M*/1000 in phosphate buffer (*M*/15 = *30* cc. + *20 cc.)* Buffer *P*H, *7.39.* T, 30°

$Na_2S_2O_4$ added cc.	*Eh* in volts Au plated Pt	Graphite	Diff. between Au and C, volts
0.03	−0.0704	−0.0691	−0.0013
.10	− .0945	− .0935	− .0010
.135	− .1013	− .1007	− .0006
.24	− .1103	− .1101	− .0002
.57	− .1248	− .1244	− .0004
.89	− .1313	− .1314	+ .0001
1.18	− .1372	− .1370	− .0002
1.52	− .1434	− .1432	− .0002
1.83	− .1486	− .1484	− .0002
2.13	− .1563	− .1560	− .0003
2.24	− .1602	− .1600	− .0002
2.34	− .1642	− .1639	− .0003
2.49	− .1742	− .1736	− .0006
2.58	− .1861	− .1854	− .0007
2.61	− .2070	− .1997	− .0073

TABLE IV

TITRATION OF INDIGO DISULFONATE WITH $Na_2S_2O_4$

M/1000 Indigo disulfonate in Sørensen's phosphate buffer (*M*/15 = *30* cc.) *20* cc. of same buffer added. Total, *50* cc. *P*H, *7.39.* T. 30°

$Na_2S_2O_4$ added cc.	*Eh* in volts Bright Pt	W	Diff. between Pt and W, volts
0.06	−0.0873	−0.0900	+0.0027
.09	− .0925	− .0925	+ .0000
.19	− .1060	− .1050	− .0010
.30	− .1132	− .1110	− .0022
.41	− .1181	− .1173	− .0008
.51	− .1221	− .1211	− .0010
.61	− .1256	− .1249	− .0007
.71	− .1281	− .1270	− .0011
.82	− .1307	− .1299	− .0008
.99	− .1347	− .1337	− .0010
1.21	− .1383	− .1385	+ .0002
1.42	− .1420	− .1417	− .0005
1.53	− .1443	− .1431	− .0012
1.66	− .1472	− .1457	− .0015
1.85	− .1506	− .1492	− .0014
2.03	− .1552	− .1534	− .0018
2.19	− .1590	− .1561	− .0029
2.38	− .1690	− .1645	− .0045
2.48	− .1750	− .1695	− .0055
2.59	− .2071	− .1812	− .0259

Tungsten gives sharp values in these dyestuff systems, but agreement with platinum is not so valuable as with graphite. Values are identical in those ranges where the dye system is particularly well poised, **i.** *e.,* 30 to 70% reduction, and in isolated instances values may be given agreeing with platinum to within ±2 millivolts from 5 to 95% reduction. Table IV portrays the usual experiment.

Hydrogen gas is without detectable effect on graphite and tungsten electrodes, and in this respect it behaves in a manner similar to mercury electrodes, since there is no measurable difference of potential whether the solution be saturated with nitrogen or hydrogen.

Conclusion

Graphite and tungsten electrodes have been tested in oxidation–reduction systems. In the quinhydrone system graphite gives results identical with those obtained at blank platinum and gold-plated platinum; whereas tungsten gives entirely different values.

In the ferro–ferricyanide system graphite gives measurements one to two millivolts less than platinum; whereas those with tungsten are 5 to 10 millivolts less.

Graphite gives the same results as platinum in a dyestuff system, be it well or poorly poised; whereas tungsten gives reliable results only when the system is well poised.

The potentials of graphite and tungsten against a reversible dye system are unaffected by change from a nitrogen to a hydrogen atmosphere.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL HYGIENE, SCHOOL OF HYGIENE AND PUBLIC HEALTH, THE JOHNS HOPKINS UNIVERSITY]

THE PREPARATION OF MANGANESE-FREE MAGNESIUM

BY ELSA R. ORENT AND O. S. RASK

RECEIVED APRIL 10, 1930 PUBLISHED JULY 3, 1930

In the course of an investigation of the possible function of manganese in animal metabolism, a number of manganese-free substances were required, among them a suitable magnesium salt. In considering magnesium salts for this purpose, it was discovered that manganese was invariably present in all of the best and C. P. labeled magnesium salts and all other magnesium preparations obtainable. Also, all magnesium compounds especially prepared with reference to freedom from manganese contained the element. The presence of manganese could be demonstrated in all these magnesium preparations by both the periodate and the spectrographic methods. Furthermore, our own efforts showed that all known methods of purifying magnesium salts were ineffective for removing such traces of manganese as could be detected by either of the above methods. The idea was then conceived of removing the manganese by first converting it into permanganate. As is well known, this can be readily done by means of potassium periodate.

The first attempt to free magnesium from manganese in the permanganate form consisted of adding in the customary manner a small amount of potassium periodate to a 10% solution of magnesium sulfate acidified with sulfuric acid and heating the resulting solution until the pink permanganate color had developed. The solution was then cooled and rendered alkaline with ammonia. The resulting precipitate of magnesium hydroxide was allowed to settle, after which the supernatant liquid was decanted as completely as possible. The precipitated magnesium hydroxide was then washed several times with distilled water which had previously been treated with sulfuric acid and potassium iodate and then rendered faintly alkaline. This procedure no doubt removed some manganese, but the magnesium hydroxide so treated always contained sufficient manganese to be detected spectrographically. Apparently, therefore, magnesium hydroxide has the capacity for adsorbing and holding in some way small amounts of manganese, which cannot be washed out. Accordingly, removal of the permanganate must take place, if at all, not after but before the magnesium hydroxide is precipitated.

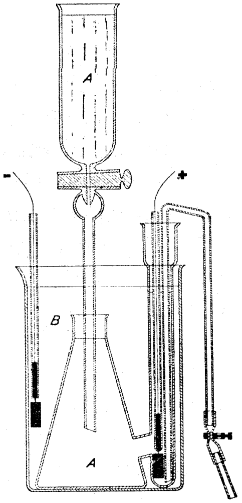

Fig. 1—A, 10% $MgSO_4$ solution; B, 0.1% $(NH_4)_2SO_4$ solution.

Electrolysis suggested itself as a possible method of separating Mg^{++} and MnO_4^- ions since they are oppositely charged and migrate to opposite poles. In a suitably designed electrolysis cell magnesium will collect as a precipitate of magnesium hydroxide at the cathode, whereas the MnO_4^- ions will concentrate at the anode. However, it is obvious that the principal consideration in the design of such a cell is an arrangement by which the original permanganate-containing solution is kept apart and separated from the cathode so that the permanganate will not be reduced by the nascent hydrogen evolved from the cathode. The design of such an arrangement was accomplished in the cell illustrated in the accompanying diagram. By means of this cell we have succeeded in preparing magnesium hydroxide which is spectrographically free from manganese. As designed and used in this Laboratory this cell consists of a two-liter pyrex beaker, a 350-ml. Erlenmeyer flask to which is fused a side arm tube in the manner indicated, a dropping funnel, a siphon tube and platinum electrodes, all assembled as indicated in the illustration. After this illustration had been prepared it was found preferable to place at a somewhat higher level the inclined tube joining the Erlenmeyer flask with the anode-containing tube. By such a design the anode pocket is made deeper, thereby making possible a more complete isolation and removal of acid hydrolysis products, *viz.*, sulfuric and permanganic acids.

Operation

The Erlenmeyer flask is filled to a level about three-fourths to one inch from its mouth with a 10% solution of magnesium sulfate (A) whose manganese has previously been oxidized to the permanganate form in the usual manner by potassium periodate. The flask is then placed inside the two-liter beaker, after which the electrodes, the siphon and the dropping funnel are placed as indicated in the figure. A 0.1% solution of ammonium sulfate (B) is then carefully introduced into the space between the beaker and the Erlenmeyer flask, including the space within the neck of the flask not filled by (over) the magnesium sulfate solution, the level of the ammonium sulfate solution being adjusted to a point about three-quarters to one inch higher than the mouth of the Erlenmeyer flask. The dropping funnel is next filled with another portion of the same 10% solution of magnesium sulfate, indicated by A in the illustration (previously treated with potassium periodate) as that already contained in the flask. Operation may now be started by connecting the electrodes directly with a 110-volt direct current, which was found suitable for this particular cell. Within a few minutes magnesium hydroxide can be observed to deposit around the cathode, which is in the space within the beaker but outside the flask. At the same time sulfuric and permanganic acids will concentrate in the pocket of the side arm containing the anode. These acids must be drawn off at approximately the same rate as they are formed in order to maintain the efficiency of the process. This removal of the acid is accomplished by means of the siphon which reaches to the bottom of the anode-containing pocket. It is difficult to ascertain with any exactness the proper rate of flow of this siphon. However, we have found by experience that a flow of 15 to 20 drops per minute yields satisfactory results in this particular cell. The rate at which the solution so withdrawn, together with the rate of electrolysis, determines the rate at which additional permanganate-containing magnesium sulfate solution must be introduced from the dropping funnel. Obviously, this rate is maintained by adjusting the drip from this funnel so that the liquid junction between the permanganate-containing magnesium sulfate solution in the Erlenmeyer flask and the overlying solution, which was originally ammonium sulfate, is approximately at the same level as at the start, that is, three-fourths to one inch from the mouth of the Erlenmeyer flask. It will usually require three or four readjustments of the stopcock in the dropping funnel before the rate of inflow through the funnel will balance the combined rates of outflow through the siphon and the electrolysis. An inflow of about 25 drops per minute will nearly strike the balance when the outflow is 15 to 20 drops and the electrolyzing current is 110 volts. When this balance has been attained, as indicated by the constancy of the level of the liquid junction between the permanganate-containing magnesium sulfate solution and the overlying solution in the neck of the Erlenmeyer flask, electrolysis will proceed with little need for attention. The above liquid junction is always so conspicuous and clear-cut that there is never any difficulty in locating it with the eye. An inspection of the cell about once an hour is sufficient. After six or seven hours, a large and voluminous drift of magnesium hydroxide will have deposited on the bottom of the beaker and this will be found spectrographically free from manganese.

Summary

Apparently all of the highest grade and C. P. labeled magnesium compounds contain traces of manganese which cannot be removed by ordinary methods of purification. A new method has been developed by which magnesium salts can be rendered manganese-free. This method consists

of an oxidation of the manganese to the permanganate form by means of potassium periodate, followed by electrolysis in a specially designed cell in which magnesium hydroxide deposits in a cathode-containing compartment and the permanganate in an anode-containing compartment. An essential feature of this cell is an arrangement whereby hydrogen from the cathode is kept out of contact with the permanganate.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXXIV. TRIMETHYL GERMANIUM BROMIDE[1]

BY L. M. DENNIS AND W. I. PATNODE

RECEIVED APRIL 16, 1930 PUBLISHED JULY 3, 1930

Halogenated aryl compounds of germanium of the type R_3GeX have been prepared by several investigators.[2] These compounds are solids which can readily be purified by crystallization from organic solvents. Comparatively little work has been done on the germanium alkyl compounds, and no halogenated alkyl of the above type has been announced. Trimethyl germanium bromide was chosen as a typical representative of this class. It was to be expected that the compound would be somewhat more difficult to prepare and purify than the corresponding aryl compounds since it probably would be a liquid that is rapidly attacked by atmospheric moisture. Consequently, the method of halogenation developed by Dennis and Judy[3] was used.

Materials.—Germanium tetrachloride was converted to germanium tetramethyl by the method of Dennis and Hance.[4] Hydrogen bromide was prepared by the reduction of bromine by hydrogen sulfide.

Procedure.—The apparatus was similar to that used by Dennis and Judy[3] for the halogenation of monogermane. Anhydrous aluminum bromide was introduced into the reaction bulb in the manner there described. About 15 g. of germanium tetramethyl was distilled into one of the smaller bulbs of the vacuum chain, after its purity had been established by determination of its vapor tension at 0°. Slightly less than the theoretical amount of hydrogen bromide required by the equation

$$HBr + Ge(CH_3)_4 = Ge(CH_3)_3Br + CH_4$$

was condensed in another bulb of the apparatus, and was then distilled over into the bulb that contained the germanium tetramethyl. The two

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[1] The work upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925); Kraus and Foster, THIS JOURNAL, **49**, 457 (1927); Orndorff, Tabern and Dennis, *ibid.*, **49**, 2512 (1927).

[3] Dennis and Judy, *ibid.*, **51**, 2321 (1929).

[4] Dennis and Hance, *J. Phys. Chem.*, *30*, 1055 (1926).

substances in vapor phase were then passed over into the reaction bulb which contained the catalyst. As soon as the vapors came in contact with the aluminum bromide on the walls of this bulb, reaction took place, as was evidenced by the formation of drops of liquid around the crystals of the catalyst. To insure thorough mixing of the two reacting substances, liquid air was alternately applied to and removed from the smaller bulb, which throughout the reaction remained in connection with the reaction bulb. The action was allowed to continue during a period of two days.

The volatile products were then distilled over into the smaller bulb by cooling it with liquid air, and the liquid was separated by distillation into two fractions, one volatile below $-100°$ and the other volatile above that temperature. The sample volatile below $-100°$ was analyzed by combustion, was found to be pure methane, and was discarded. The other portion was separated into three fractions by distillation, following the general method described by Dennis, Corey and Moore.[5] The greater part of the liquid showed a vapor tension at 0° of from 4.7 to 5.1 mm. This portion was again fractionated, the middle fraction was separated by further fractional distillation into small portions, and the vapor tension of each at 0° was determined. A constant value of 4.9 mm. was obtained and consequently these several small fractions were combined.

Analysis.—A sample was distilled over into a tube that was provided at its upper end with a wide slip-joint carrying a stopcock and a normal slip-joint above that for attaching it to the chain. This tube was detached and weighed to determine the weight of the sample, the liquid in it was then frozen and the large slip-joint was removed. Water and a few drops of nitric acid were added and the mixture was allowed to warm up while being gently shaken. The substance rapidly dissolved. A solution of silver nitrate was then added in excess and the silver bromide was collected on a filter and weighed.

Carbon and hydrogen were determined by the combustion method devised by Dennis and Hance,[4] the bromine in the sample being stopped by **a** plug of silver turnings.

Germanium was determined by slowly dropping a sample of the liquid from a pipet onto a warm mixture of 90 parts of sodium peroxide and 10 parts of sodium carbonate. The mass was allowed to cool, was then heated with dilute hydrochloric acid, and the solution was made 6 N with respect to hydrochloric acid. The germanium in this solution was now determined by the method of Johnson and Dennis.[6]

Analyses

Bromine.—Subs., 0.1943, 0.3141. **Calcd.** for $Ge(CH_3)_3Br$: Br, 0.0785, 0.1270, 40.44%. Found: Br, 0.0786, 40.45%. 0.1274, 40.54%.

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[5] Dennis, Corey and Moore, THIS JOURNAL, 46, 657 (1924)

[6] Johnson and Dennis, *ibid.*, **47,** 790 (1925).

Germanium.—Subs., 0.4101, 0.1437. Calcd. for $Ge(CH_3)_3Br$: Ge, 0.1506, 0.0528, 36.74%. Found: Ge, 0.1532, 37.35%, 0.0525, 36.52%.

Carbon and Hydrogen.—Subs., 0.8214, 0.2749. Calcd. for $Ge(CH_3)_3Br$: C, 0.1497, 0.0501, 18.23%; H, 0.0377, 0.0126, 4.59%. Found: C, 0.1485, 18.09%, 0.0503, 18.29%; H, 0.0380, 4.74%, 0.0125, 4.55%.

Physical Properties

Melting Point.—The melting point of trimethyl germanium bromide, determined by the dropping ring method of Dennis, Corey and Moore,[5] is −25".

Liquid **Density.**—The liquid density of trimethyl germanium bromide is 1.544 g./cc. at 18°.

Vapor Density and Molecular **Weight.**—The vapor density was determined by the method of Victor Meyer using the apparatus as modified by Weiser.[7] The tube was heated by the vapor of boiling ethylene glycol contained in the outer jacket, and the displaced air was measured in a Hempel gas buret. Wt. 1 liter (corr.) 8.963, 9.220. Mol. wt. (av.), 203.6. Calcd., 197.6.

Refractive Index.—The refractive index of trimethyl germanium bromide is 1.4705 at 18°.

Vapor Tension.—The vapor tension curve was determined by the method of Laubengayer and Corey.[8]

Temp., °C.	−25 0	−6 2	+3.7	23.4	32 2	41.5	46 0	52.5	
Press., mm.	0.1	2 9	7.1	21.4	32.8	50.9	62.3	82.5	
Temp., °C.	58.4	63 8	66 0	74 2	77.8	80.5	85.4	89 0	94.4
Press., mm.	1088	1318	150.6	195.0	222.7	2456	301.1	337.0	398.1
Temp., °C.	95.5	98 5	101 1	105.5	108.9	113.2	115.7	119.7	
Press., mm.	415 5	447.0	495.5	555 9	619 5	711.2	787.1	881.0	

The general equation as determined from the above data is

$$\log_{10} p = -1956 \times \frac{1}{T,\ OK} + 7.912$$

Boiling Point.—The boiling point as taken from the vapor tension curve is 113.7°.

The material is a colorless oily liquid with a characteristic odor resembling turpentine and onions. It is soluble in the usual organic solvents.

Chemical Properties

Trimethyl germanium bromide is hydrolyzed by water. Silver bromide can be precipitated from this solution by the addition of a solution of silver nitrate. The product of hydrolysis is a volatile liquid. Germanium disulfide is not precipitated when an aqueous solution of trimethyl germanium bromide is acidified and treated with hydrogen sulfide. This is presumably due to the formation of a non-polar hydroxyl compound.

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[7] Weiser, *J. Phys. Chem.*, 20, 532 (1916).

[8] Laubengayer and Corey, *ibid.*, 3C, 1043 (1926).

$$Ge(CH_3)_3Br + HOH = Ge(CH_3)_3OH + HBr$$

This hydroxyl derivative may or may not condense with itself with the elimination of a molecule of water. The corresponding phenyl compound does, however.[9] Trimethyl germanium bromide is rapidly oxidized by sodium peroxide and by hot chromic acid, but only slowly by ammoniacal 30% hydrogen peroxide. Hot, concentrated sulfuric acid liberates bromine.

When a sample was dissolved in benzene and dry ammonia gas was bubbled through the solution, a white crystalline precipitate appeared. This was shown by analysis to be ammonium bromide. The filtrate from this precipitate was allowed to evaporate at room temperature. When only a few drops remained, the material had an odor similar to that of the original material. However, when a drop on a stirring rod was brought in contact with a drop of water, the odor of ammonia was noticed. This liquid fumed strongly when concentrated hydrochloric acid was added. It is assumed from this experiment that trimethyl germanium bromide reacts with ammonia to form an amine which is volatile and readily hydrolyzed by water.

Summary

The preparation, purification and some chemical and physical properties of trimethyl germanium bromide are described.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE SEPARATION OF EUROPIUM BY ELECTROLYTIC REDUCTION. OBSERVATIONS ON THE RARE EARTHS. XXXV

BY L. F. YNTEMA

RECEIVED APRIL 18, 1930 PUBLISHED JULY 3, 1930

The existence of a bivalent europium chloride was announced by Urbain and Burion[1] who prepared it by reduction of the anhydrous trichloride with hydrogen at 400–450°. Jantsch, Alber and Grubitsch[2] extended the study of the bivalent compounds of europium. They found that europium bichloride is quite stable in solution. The bi-iodide was found to be still more stable. The sulfate is a fine, white crystalline compound, insoluble in water and difficultly soluble in acids. The bichloride of samarium, described by Matignon and Cazes[3] and by Jantsch, Rüping and Kunze,[4] reacts with water and, more rapidly, with acids, evolving hydrogen and undergoing oxidation to the trivalent state. The bivalent sulfate is a red compound, sparingly soluble.

[9] Morgan and Drew, J. *Chem. Soc.*, 127, 1760 (1925).

[1] Urbain and Burion, *Compt. rend.*, 153, 1155 (1911).

[2] Jantsch, Alber and Grubitsch, *Monatsh.*, 53, 54, 305 (1929).

[3] Matignon and Cazes, *Compt. rend.*, 142, 83 (1906).

[4] Jantsch, Rüping and Kunze, *Z. anorg. allgem. Chem.*, 161, 210 (1927).

These facts suggested the possibility of separating europium from the other rare earths by electrolytic reduction in the presence of the sulfate ion.

I. Experimental Procedure

Five grams of mixed rare earth oxides containing samarium, europium and a small percentage of gadolinium was dissolved in hydrochloric acid. The excess acid was evaporated and the solution was diluted to 125 cc.; 2 cc. of sulfuric acid (sp. gr. 1.84) was added. It was found that the addition of more sulfuric acid would result in the precipitation of trivalent sulfates. Visual examination of the solution through a seven-centimeter layer showed the absorption spectra of samarium and of europium.

This solution was put into the cathode compartment of the electrolytic cell (Fig. 1). The anode compartment was filled to the same level with dilute sulfuric acid of approximately molar concentration. A current of 0.18 ampere, corresponding to a current density at the cathode of 0.01 amp./sq. cm., was used. The voltage drop between electrodes was 65 volts.

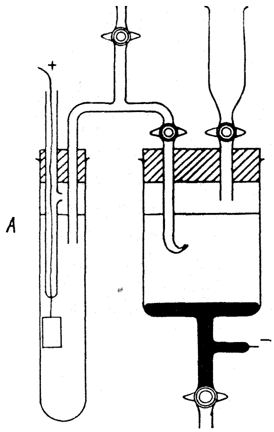

Fig. 1.—The electrolytic cell. C, Cathode compartment with mercury cathode; A, anode compartment with platinum anode.

After electrolyzing for six hours, an appreciable amount of a granular, white precipitate, later identified as bivalent europium sulfate, had formed. This was removed for analysis. On continuing the electrolysis more precipitate was formed. After electrolyzing for about twenty-four hours, no more appeared and the reduction was assumed to be complete. The solution now showed none of the absorption bands of europium.

II. Analysis

(a) Gravimetric.—The portion of the precipitate reserved for analysis was collected in two portions for duplicate analyses on sintered glass crucibles. The precipitate was washed with air-free water until the washings gave no precipitate with ammonium hydroxide, then with alcohol and finally with anhydrous ether. It was dried at 65°. After weighing, it was again heated at the same temperature for an hour; no gain or loss in weight occurred.

The europium sulfate was then dissolved in dilute nitric acid. The reaction with nitric acid yielded nitrogen dioxide, indicating that an oxidation occurred. The spectrum of this solution showed the absorption bands of europium and none of samarium. After diluting the nitric acid solution to 150 cc., the excess acid was neutralized with ammonium hydroxide and the solution was then made acid with nitric acid, two or three drops of concentrated acid in excess being added. The europium was precipitated as oxalate, ignited and weighed as oxide. The oxide obtained was a very pale pink in color. The sulfate was determined as barium sulfate. The results of the analysis are given in Table I. The precipitate is shown to have the composition $EuSO_4$.

TABLE I

ANALYSIS OF PRECIPITATED EUROPIUM SULFATE

		I	II
1	Weight of $EuSO_4$ taken, g.	0.2128	0.1388
2	Weight of Eu_2O_3 found, g.	.1476	.0963
3	Weight of $BaSO_4$ found, g.	.2053	.1327
4	Weight of Eu (calcd. from No. 2), g.	.1275	.0832
5	Weight of SO_4 (calcd. from No. 3), g.	.0845	.0546
6	Weight of $EuSO_4$ found (4 plus 5), g.	.2120	.1378
7	Percentage error	0.4	0.7
8	Mol. ratio SO_4/Eu	1.049	1.039

(b) Spectroscopic.—Photographs of the arc spectra on carbon electrodes of (1) the original mixed oxides, (2) the oxide obtained in analysis No. 1 and (3) of an oxide prepared from the solution after electrolysis, were made. A Hilger E I quartz prism spectrograph was used. It was found that the precipitate consisted of europium with very little samarium (estimated at 1 or 2%). The solution after electrolysis was almost europium free. The presence of samarium in the precipitate may have been due either to a partial reduction or the mechanical inclusion by the precipitate.

The writer wishes to express his appreciation of the assistance of Mr. P. W. Selwood, who photographed the spectra.

Summary

1. Bivalent europium sulfate may be precipitated from an acid solution by electrolytic reduction in the presence of the sulfate ion.

2. An analysis of the precipitate showed it to have the composition represented by the formula $EuSO_4$. This is a white crystalline compound, stable when heated in air at 65°, and insoluble in dilute acids. It is oxidized by dilute nitric acid.

3. Visual examination of the solution of the precipitate in nitric acid shows no samarium absorption bands. The solution after electrolysis showed none of the europium absorption bands.

4. The arc spectrum of the precipitated fraction indicates that it consists of europium with very little samarium. The solution is almost samarium free.

The use of this reaction for the isolation and the purification of europium is being further investigated.

URBANA, ILLINOIS

[Contribution from the Cobb Chemical Laboratory, University of Virginia, No. 59]

THE ADSORPTION OF ARSENIOUS ACID BY HYDROUS FERRIC OXIDE

By John H. Yoe

Received April 21, 1930 Published July 3, 1930

Almost a century ago Bunsen and Berthold[1] observed that freshly precipitated ferric oxide had the power of removing arsenious acid from solution and considered the action as due to the formation of a basic ferric arsenite. A similar view was later held by Reychler.[2] On the other hand, Biltz[3] and Boswell and Dickson[4] considered the action as due to adsorption and expressed their results approximately by the adsorption equation $X = kC^{1/n}$, where X is concentration of arsenious oxide on the ferric oxide, C is concentration of arsenious oxide at equilibrium, and k and n are constants. Lockemann[5] and his co-workers have studied the conditions under which arsenious acid is completely removed from solution and they varied the amounts of both adsorbent and arsenic, as well as the temperature. Moreover, each adsorption was measured at the temperature at which the adsorbent was formed.

Since the adsorption power is altered by various factors such as (1) temperature at which the hydrous oxide is formed, (2) the temperature at which adsorption takes place, **(3)** rate of formation of the adsorbent, etc., it seemed desirable to study the adsorption under a definite set of conditions. In general, the experimental conditions and procedure were the same as those employed in a similar investigation of the adsorption of arsenious acid by hydrous aluminum oxide.[6]

Experimental Part

Rate of Adsorption.—A series of adsorptions was carried out at 25° using hydrous ferric oxide formed at the same temperature, and the adsorption period was varied from a few minutes to forty-two hours. The results are recorded graphically in Fig. 1, where the millimoles of arsenious oxide adsorbed by a given amount of hydrous ferric oxide (corresponding to 0.250 g. of Fe_2O_3) have been plotted as ordinates, and the total times in hours as abscissas.

Adsorption of Arsenious Acid by Hydrous Ferric Oxide Formed at Various **Tem-**

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[1] Bunsen and Berthold, "Das Eisenoxydhydrat, ein Gegengift der arsenigen Säure," Gottingen, 1834; *cf.* Guibourt, *Arch. Pharm.*, [2] 23, 69 (1840).

[2] Reychler, J. *chim. phys.*, 7, 362 (1909); 8, 10 (1910); *cf.* Oryng, *Kolloid-Z.*, 22, 149 (1918).

[3] Biltz, *Ber* , 37, 3138 (1904); *J. chim. phys.*, *7*, 570 (1909); *cf. Kolloid-Z.*, 26, 179 (1920).

[4] Boswell and Dickson, This Journal, 40, 1793 (1918).

[5] Lockemann and Paucke, *Kolloid-Z.*, 8, 273 (1911); Lockemann and Lucius, *Z. physik. Chem.*, 83, 735 (1913).

[6] Yoe, This Journal, 46,2390 (1924).

peratures.—Two series of measurements were made using oxides precipitated at 0, 25. 50, 75 and 100°, respectively. The concentration of the arsenious acid in each series varied from about 0 9 to 4.5 millimoles of As_2O_3 per 250 cc. All adsorptions were carried out at 25°. One series was run at an adsorption period of forty-two hours and another at a thirty-day period. The rate of adsorption previously determined had shown that an approximate equilibrium point is reached at the end of twelve hours and that adsorption at the end of forty-two hours was identical (within the limits of accuracy) with the twelve-hour period. The results are shown graphically in Figs. 2 and 3, where millimoles of arsenic trioxide adsorbed by a given amount of hydrous ferric oxide (corresponding to 0.250 g. of Fe_2O_3) are plotted as ordinates, and the temperatures at which the oxides were formed as abscissas.

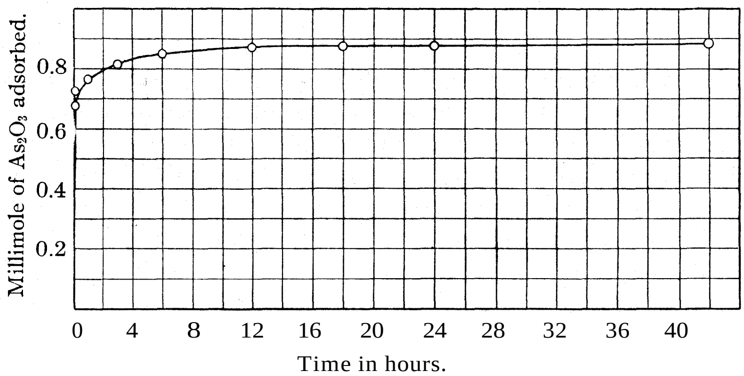

Fig. 1.—Rate of adsorption of arsenious acid by hydrous ferric oxide at 25°.

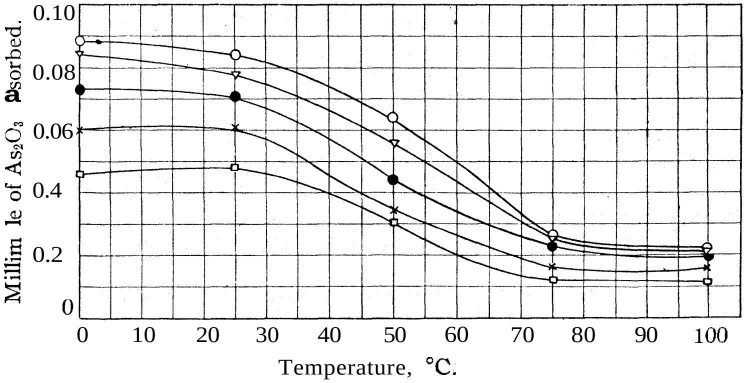

Fig. 2.—Adsorption of arsenious acid by hydrous ferric oxide formed at various temperatures (adsorption time, 42 hours).

Adsorption Isotherms.—Adsorption isotherms were obtained for hydrous ferric oxides formed at temperatures of 0, 25, 50, 75 and 100°, respectively, and for the oxide formed at 100° and boiled for twenty-four hours under a reflux condenser. One series of isotherms was run at an adsorption period of forty-two hours and another at a thirty-day period. All measurements were made at 25°. The data are given in Figs. 4 and 5, where the ordinates show the millimoles of arsenious oxide adsorbed by a given amount of hydrous ferric oxide (corresponding to 0.250 g. of Fe_2O_3), and the abscissss the millimoles of arsenious oxide unadsorbed. The corresponding logarithmic plots are given in Figs. 6 and 7.

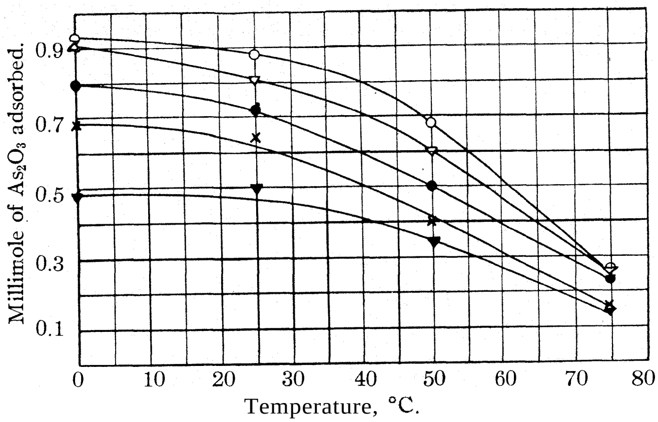

Fig. 3.—Adsorption of arsenious acid by hydrous ferric oxide formed at various temperatures (adsorption time, 30 days).

Discussion of Experimental Data

Rate of Adsorption.—As seen in Fig. 1, the rate of adsorption is quite rapid, about 75% of the total adsorption taking place within the first five minutes. At the end of twelve hours 0.871 millimole of arsenious oxide had been adsorbed and 0.885 millimole at the end of forty-two hours.

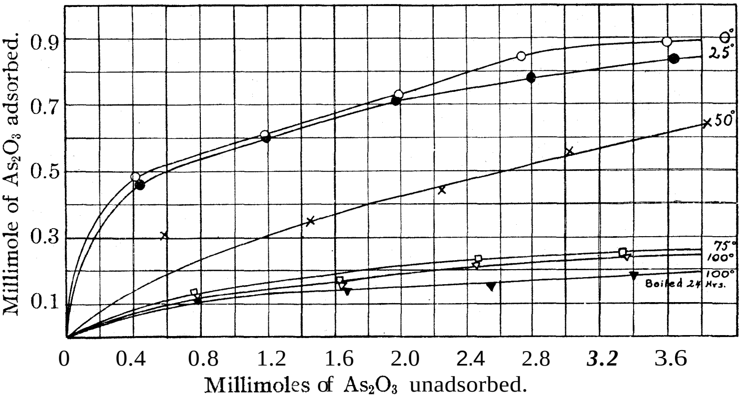

Fig. 4.—Adsorption isotherms of arsenious acid on hydrous ferric oxide at 25° (adsorption time, 42 hours).

The run was discontinued at the end of forty-two hours since it was evident that at least an approximate equilibrium had been reached. That there is a very slight continued adsorption was observed later when determining the adsorption isotherms. For instance, one run with the hydrous ferric oxide formed at 25° gave an adsorption value of 0.84 millimole at the end of forty-two hours and 0.88 millimole at the end of thirty

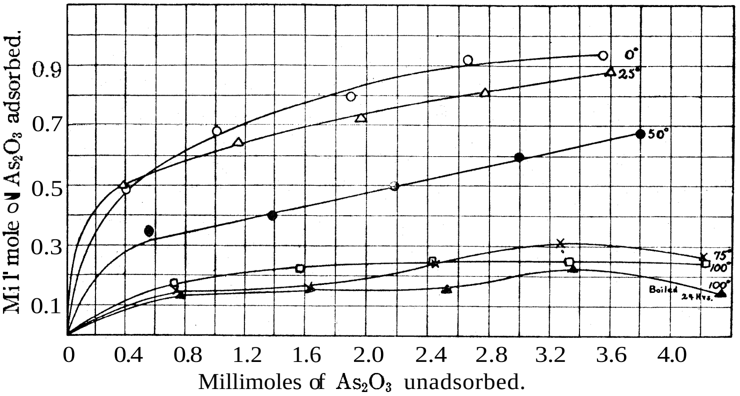

Fig. 5.—Adsorption isotherms of arsenious acid on hydrous ferric oxide at 25° (adsorption time, 30 days).

days, an increase of only 0.04 millimole. This slight increase in adsorption of the thirty-day period over the forty-two-hour period was shown in all

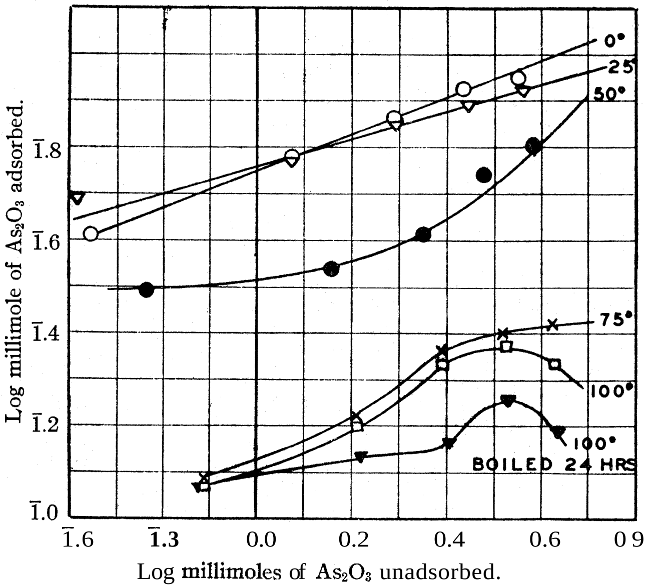

Fig. 6.—Logarithmic plot of curves in Fig. 4.

cases, regardless of the temperature (0 to 100°) at which the hydrous ferric oxide was formed and the concentration (0.9 to 4.5 millimoles per 250 cc.)

of the arsenious acid. The increase in adsorption varied from about 0.01 to 0.08 millimole, but was usually about 0.04 millimole. Hydrous aluminum oxide shows a similar slow increase in adsorption. Several explanations have been suggested.[6]

Adsorption of Arsenious Acid by Hydrous Ferric Oxide Formed at Various Temperatures.—The adsorption power of the hydrous ferric oxide decreases, the higher the temperature at which it is formed. The effect is much greater over the range from 0 to 75° than from 75 to 100°. The marked effect of boiling on the adsorption power of the hydrous oxide is shown by the fact that precipitating at 100° and then boiling under a reflux condenser for twenty-four hours cut down the adsorption power more than 30% of that precipitated at 100° but not boiled. Adsorption by the hydrous oxide precipitated at 0° is about 4.2 times greater than by that formed at 100° and about 5.8 times greater than that of the hydrous oxide precipitated at 100° and refluxed for twenty-four hours. The effect of raising the temperature of formation, therefore, is to decrease the adsorption power of the hydrous oxide, which is in agreement with results previously obtained with hydrous aluminum oxide.[6]

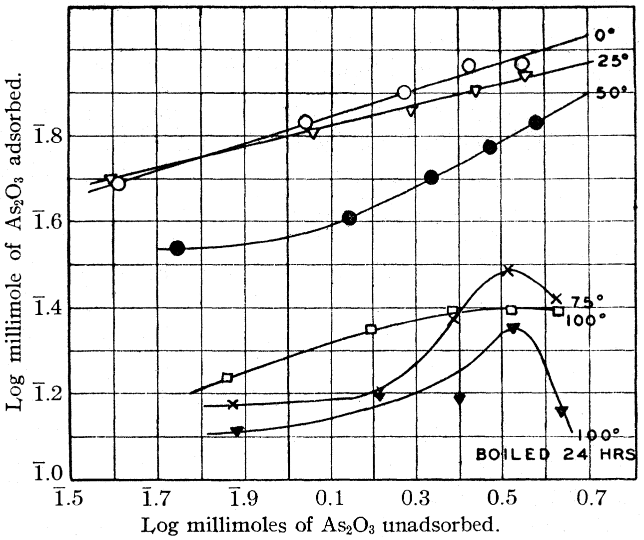

Fig. 7.—Logarithmic plot of curves in Fig. 5.

Adsorption Isotherms.—Since the rate curve had shown that between twelve and forty-two hours adsorption is constant or at least very nearly so, a concentration function or adsorption isotherm was obtained for a forty-two-hour period for each lot of hydrous ferric oxide formed at the various temperatures ranging from 0 to 100°. Corresponding isotherms were also measured for a thirty-day period, As noted in Figs. 4 and 5, the points fall on smooth curves, each curve lying below the preceding one—the one for 0° formation being the highest and that for precipitation at 100° and boiling for twenty-four hours being the lowest and almost flat. When logarithmic plots are made (see Figs. 6 and 7) some striking results are noted. The hydrous oxides formed at 0 and at 25° give straight lines, and hence the adsorption may be expressed by the adsorption equation $X = kC^{1/n}$. The curves for the hydrous oxide formed at 50° deviate from a straight line and are convex to the x-axis, while those for the oxides formed at higher temperatures are concave to the x-axis. It is obvious that the phenomenon of adsorption by these oxides cannot be expressed by the simple adsorption equation. The data also show considerable deviation from Langmuir's equation.

Summary

1. The rate of adsorption at 25° of arsenious acid by hydrous ferric oxide is very rapid, 75% or more of the adsorption taking place within the first few minutes. An apparent or approximate equilibrium was reached in about twelve hours but at the end of thirty days a very slight further adsorption had taken place.

2. Hydrous ferric oxides have been formed under a definite set of conditions and at 0, 25, 50, 75 and 100°, respectively, and at 100° and boiled gently under a reflux condenser for twenty-four hours. Adsorption isotherms at 25° have been obtained for each of these oxides with arsenious acid. Those formed at 0 and at 25° follow the simple adsorption equation, $X = kC^{1/n}$. The hydrous oxides formed at higher temperatures show considerable deviation from the simple adsorption equation, as well as from Langmuir's equation.

3. The adsorption power of hydrous ferric oxide for arsenious acid decreases the higher the temperature at which it is formed. Gentle boiling under a reflux condenser for twenty-four hours greatly reduces the adsorption capacity. These results are in good agreement with similar ones obtained with hydrous aluminum oxide.

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[CONTRIBUTION NO. 629 OF THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

THE SOLUBILITY OF LEAD IODATE IN WATER AND IN 0.1 *N* SALT SOLUTIONS

BY VICTOR K. LA MER AND FREDERICK H. GOLDMAN

RECEIVED MAY 5, 1930 PUBLISHED JULY 3, 1930

In connection with our studies[1] on the solubilities of lanthanum and thallous iodates in salt solutions we also considered making similar measurements upon lead iodate as an example of a (2, —1) type saturating salt. Unfortunately experimental difficulties such as inability readily to reproduce the water solubility with the high precision desired (0.1%) for testing the principle of specific interaction, and the limited range of concentration for which sulfate solvents could be employed, led us to discontinue the more complete study in favor of $TlIO_3$. The final solubility value for $Pb(IO_3)_2$ in water was $3.61 \cdot 10^{-5}$ moles/liter at 25°, which is considerably lower than the value of $5.51 \cdot 10^{-5}$ reported by Harkins and Winninghoff[2] or the value $4.13 \cdot 10^{-5}$ moles/liter reported by Kohlrausch[3] for 25.77°.

Preparation of **Lead** Iodate.—One hundred and twenty grams (0.216 mole) of lead iodate was precipitated by simultaneous dropwise addition of equivalent solutions of C. P. lead nitrate and potassium iodate in a 23-liter jar filled with water under constant stirring at about 60°. The supernatant liquid was replaced with fresh water eight times during the precipitation process, which occupied several days' time. The potassium nitrate resulting from metathesis therefore did not exceed 0.002 M at any time. It has been our experience that higher solubilities are usually obtained when salts are precipitated from more concentrated solutions, due we believe to occlusion of metathetic products. Harkins and Winninghof gave no details other than that their salt was precipitated in very dilute solution in which the nitrate was constantly in excess. Our product was of a very light cream color and of a fineness resembling talcum powder.

Results.—The lead iodate was placed in the solubility tubes, described previously,[4] in January, 1927, and washed with water or salt solutions continuously until July, 1927, with the following results for $S \cdot 10^5$, **3.68, 3.63** and 3.66 on 1/21, 1/22 and 1/23, respectively. On 1/24, $10^5 S$ suddenly rose to **3.82** and the salt assumed a light yellow color, due we believe to the liberation of traces of iodine by some accidental impurity. By continuous washing the yellow color slowly disappeared until on 4/14, $10^5 S$ had fallen to 3.60, rising to 3.61 on 6/4. During this period equilibrium was ap-

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[1] *La Mer and* Goldman, THIS JOURNAL, 51,2632 (1929).

[2] Harkins *and Winninghoff, ibid.*, **33,** 1830 (1911). *Solubility determined by direct analysis.*

[3] *Kohlrausch, Z physik. Chem.*, 46, 521–619 (1923). *Solubility determined by conductivity method.*

[4] *La Mer and Mason, THIS* JOURNAL, *49,* **363** (1927).

proached from supersaturation as well as undersaturation without producing significant differences in the results. Since both impurities and abnormally small crystals will produce a greater solubility, we feel justified in attributing more weight to our lower value than to the higher values of previous investigators. The analysis was carried out by adding **3** g. of potassium iodide to a 200-cc. aliquot of saturated solution in a 500-cc. iodine flask. Two cc. of 50% sulfuric acid was then added and the contents titrated after ten minutes with dilute thiosulfate from a weight buret. Although the precipitate formed interfered somewhat in the ease of reading the starch end-point, duplicate determinations usually checked to 0.2%.

The data in the table show that the solubilities in the potassium and sodium solvents with the same anion are almost identical, in agreement with the requirements of the principle of specific interaction since the osmotic properties (freezing-point lowerings) of potassium and sodium iodates are also almost identical[5] at 0.1 N. On the other hand, marked differences exist between the nitrates and chlorides, lead iodate like thallous iodate being more soluble in chlorides than in nitrates. This is opposite to what is usually observed and we attribute the greater solubility to the formation of complex chlorides. In the case of lead, complexes of the type $PbCl_3^-$ have been isolated at high chloride concentrations.[6] The Debye–Hiickel limit-

TABLE I

SOLUBILITY AND ACTIVITY COEFFICIENTS OF LEAD IODATE AT 25°

Solvent	Date	Final detns. avgd.	$S \cdot 10^5$ mole/liter	Log S/S_0	$-$Log f	$\sqrt{\mu}$	a_{1st} Å. units
H_2O	6/4	5	3.608	0.000	0.0105	0.0104	....
0.1 *M* $NaNO_3$	5/16	3	6.99	.287	.297	.3165	+0.72
0.1 *M* KNO_3	5/25	3	6.94	.284	.294	.3165	+0.82
0.1 *M* KCl	6/14	4	8.29	.361	.371	.3165	−1.34
0.1 *M* NaCl	7/8	4	8.30	.362	.372	.3165	−1.36

TABLE II

RECALCULATIONS OF THE DATA OF HARKINS AND WINNINGHOX

Solvent	$S \cdot 10^5$ mole/liter	Log S/S_0	$-$Log f	$\sqrt{\mu}$
H_2O	5.511	0.000	0.013	0.0128
KNO_3 0 002 M	5.71	.015	.028	.0466
0.010 *M*	6.52	.073	.086	.102
0.050 M	10.18	.267	.280	.224
0.200 M	12.71	.363	.376	.477

a_{1st} refers to the "a" value calculated using the first or Debye–Hiickel approximation of the solution of the Poisson–Boltzmann equation. See Gronwall, La Mer and Sandved, *Physik.* Z., 29, 358 (1928) for mathematical details regarding the higher approximations. μ is the ionic strength, *i. e.*, $^1/_2\, \Sigma c_i z_i^2$.

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[5] See Ref. 1, p. 2642, for more details and for references to Brönsted's papers where this relation is developed.

[6] Kendall and Sloan, THIS JOURNAL, 47,2306 (1925).

ing law predicts a value of $-\log f = 0.319$ in the 0.1 M solvents, and the last column gives the values of the parameter "a" in Å. units required by this theory. The values of "a" are absurdly small for the nitrates, which is frequently the case, but are actually negative in the case of chlorides, which is unusual for low valence chloride salts in water.

Summary

The solubility of lead iodate is $3.61 \cdot 10^{-5}$ mole/liter at 25°. The greater solubility in 0.1 N chlorides than in the nitrates of sodium and potassium is attributed to complex chloride formation.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE EFFECT OF IODINE CHLORIDE ON THE PHOTOSYNTHESIS OF HYDROCHLORIC ACID

BY G. K. ROLLEFSON AND F. E. LINDQUIST

RECEIVED MAY 5, 1930 PUBLISHED JULY 3, 1930

In recent discussions of the mechanism of the photosynthesis of hydrochloric acid it has been generally accepted that the action of the light which initiates the chain is to dissociate a chlorine molecule into a normal chlorine atom and one excited to the $^2P_1$ state. A recent paper by Rollefson[1] discussed grounds for believing that it is the excited atoms which start the reaction, the normal ones having no effect. It is highly desirable, therefore, to carry out experiments in which only one of the two kinds of atoms is produced and to see if the reaction will start under such conditions. For such experiments to be of significance it is necessary that the atoms shall be produced with as little disturbance to the other molecules as possible. The most obvious way to do this is to dissociate some molecule by light. In this case it is possible to do it by introducing iodine monochloride into the mixture of hydrogen and chlorine and it is the purpose of this paper to present experiments dealing with the behavior of such a system.

The absorption spectrum of iodine chloride has been studied by Gibson and Ramsperger,[2] who found a series of bands converging at $\nu = 17{,}410$ cm.$^{-1}$ ($\lambda = 5744$ Å.) similar in character to the bands which have been observed in the halogens by Mecke[3] and Kuhn.[4] In the case of the halogens it was shown that the convergence corresponded to a dissociation into a normal and an excited atom. The thermal data available for iodine chloride are not sufficiently accurate to say definitely whether the observed convergence corresponds to a dissociation into two normal atoms or into a

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[1] Rollefson, THIS JOURNAL, 51, 770 (1929).

[2] Gibson and Ramsperger, *Phys. Rev.*, 30, 598 (1927).

[3] Mecke, *Ann. Physik*, 71, 104 (1923).

[4] Kuhn, *Z. Physik*, **39**, 77 (1926).

normal iodine atom and an excited chlorine atom. Gibson and Ramsperger adopted the first of these two interpretations, their arguments being based on considerations of the stability of iodine chloride and also on the observation of two faint band heads at higher frequencies than the above-mentioned convergence which might be considered as part of a system corresponding to the second process. Gibson[5] later abandoned this view in favor of the dissociation into a normal iodine atom and excited chlorine atom. Whichever interpretation is correct, the fact that there is one well-defined band series in the absorption indicates that this compound can be used to supply one kind of chlorine atoms.

Preliminary experiments showed that no reaction occurred if a mixture of iodine chloride and hydrogen was illuminated at room temperature. This result tells us merely that the kind of chlorine atoms obtained in these experiments will not react directly with hydrogen. It does not exclude the possibility of these atoms starting chains by going through a Cl_3 stage, as postulated by Cremer,[6] if chlorine molecules are present. The principal experiments were therefore performed with mixtures of chlorine, iodine chloride and hydrogen.

Experimental

The reaction was carried out in a cylindrical pyrex vessel, 6 X 17.5 cm., with a polished window at one end; the other end was drawn down and sealed to a smaller tube in order that the vessel might easily be attached to the line, and a side tube of approximate dimensions 1 X 13 cm. was sealed onto the vessel at about the middle. The purpose of the side tube was to freeze out such gases as hydrochloric acid, chlorine, etc., in order that the pressure of hydrogen might be measured and the reaction followed in this way. Liquid air was used to freeze out the above-mentioned gases and a manometer containing concentrated sulfuric acid was used to measure the pressure of hydrogen. The manometer was so arranged that, during the addition of the reacting substances to the vessel, its high vacuum side could be cut off from the main line by means of a pyrex stopcock. In order to assure the maintenance of a high vacuum on this side of the manometer after the addition of the reactants, the stopcock was opened, thereby allowing the high vacuum side of the manometer to be continually pumped on by a mercury diffusion pump which was backed up by an oil pump. Before admitting the reacting gases to the vessel, the entire system was evacuated by means of the above-mentioned pumping system. The hydrogen used was prepared by the electrolysis of a concentrated solution of potassium hydroxide. The gas, after being generated, was passed over metallic copper at a temperature of approximately 300° in order to remove any oxygen that might have been present, then over phosphorus pentoxide, then through a liquid air trap to a U in the line surrounded by a mixture of solid carbon dioxide and acetone, and from this U through a capillary tube into the reaction vessel. The capillary tube was placed in the line between the U, surrounded by the solid carbon dioxide–acetone mixture, and the reaction vessel in order to prevent the iodine chloride from diffusing from the reaction vessel to the cold U during the experimental work. During the addition of hydrogen the side tube was surrounded with liquid air and the pressure of hydro-

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[5] Gibson, *Z. Physik.*, 50, 692 (1928); Gibson and Rice, ***Nature,*** 123, 347 (1929).

[6] Cremer, *Z. physik. Chem*, 128,285 (1927).

gen added was taken as the initial hydrogen pressure reading. The liquid air was then removed and chlorine was admitted to the reaction vessel. The chlorine was prepared by heating anhydrous cupric chloride, which was kept in a tube sealed on the line between the liquid-air trap and the solid carbon dioxide–acetone U. In this way the chlorine passed through the cold U, through the capillary tube, into the reaction vessel. The iodine chloride was prepared by direct reaction of iodine and chlorine in the reaction vessel. The iodine used was sublimed twice and then condensed in small tubes which had been drawn off to a fine capillary. After the iodine was condensed, the tubes were sealed off and laid aside for use. When iodine was to be introduced into the reaction vessel, one of these tubes was placed in a side tube where it could be broken by a magnetic hammer. The iodine was allowed to distil into the reaction vessel. In this way, the iodine was resublimed three times and a pure product was assured. When sufficient iodine had been introduced into the vessel, the magnetic hammer arrangement was sealed off and hydrogen and chlorine were introduced into the vessel. This mixture of gases was exposed to the light for a period of an hour or longer; then the side tube was surrounded by liquid air, and the gases, with the exception of hydrogen, were frozen out. The liquid air was then replaced by a mixture of solid carbon dioxide–acetone, which allowed the chlorine and hydrochloric acid to evaporate, keeping the iodine chloride in the solid state as iodine trichloride. The gases were pumped off and the system again evacuated. Hydrogen and chlorine were again added, in the manner previously described, and a series of measurements was made. The vessel was illuminated by means of a 500-watt projection lamp, the light from which was concentrated by a lens and passed through a quinine sulfate filter onto the plane window. The gases were exposed to the light for a definite length of time and then the amount of hydrochloric acid formed was determined by freezing out the gases and measuring the pressure of residual hydrogen. The rate of the reaction was followed by taking a series of such measurements. The iodine chloride pressure was varied by pumping out a certain fraction of the total gases and then adding hydrogen and chlorine to the remaining gases until approximately the original pressures of hydrogen and chlorine were reached. A series of points was again obtained, as described above, and by making a series of such runs, the effect of iodine chloride on the rate of the reaction between hydrogen and chlorine was studied.

In all the experiments a large excess of chlorine was used so that no large error was introduced by considering the chlorine pressure as constant during the run. Under such conditions the law for the rate of formation of hydrochloric acid is

$$\frac{\mathrm{d(HCl)}}{\mathrm{d}t} = k(\mathrm{Cl_2})(\mathrm{H_2}) = k'(\mathrm{H_2}) = -\frac{1}{2}\frac{\mathrm{d(H_2)}}{\mathrm{d}t}$$

where $k' = k(\mathrm{Cl_2})$. Integrating we find that log $(\mathrm{H_2})$ should be proportional to the time; therefore if we plot log $(\mathrm{H_2})$ against time the slope of the curve gives us the value of k'. A set of curves obtained at various iodine chloride pressures[7] is shown in Fig. 1. The straightness of the lines shows the validity of the assumptions over the range studied. The variation of k' with the iodine chloride pressure is shown in Fig. 2, where values of k' have been plotted against the square root of the reciprocal of the pressure of iodine chloride. This was found, by trial, to be the best linear plot which could be obtained, although even in this case the deviations are

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[7] The pressure unit is cm. of sulfuric acid.

fairly large at low pressures. Such deviations are not surprising, as at low pressures there is apt to be considerable uncertainty in the iodine chloride pressure. The general reproducibility of the results is shown by the fact that the points used in making this graph are from two different sets of runs; the dots are from one series and the circles from the other.

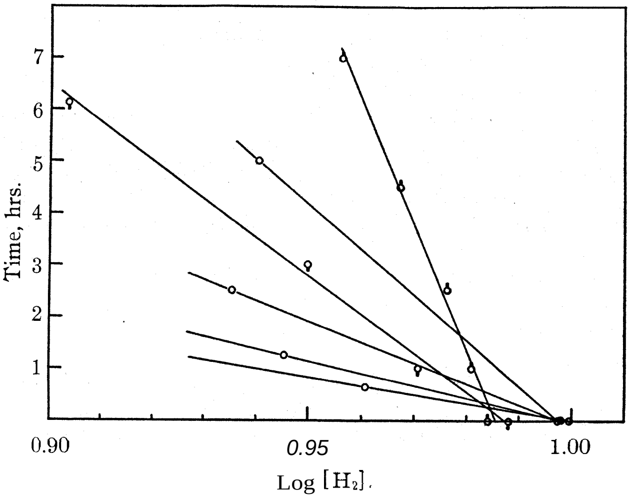

Fig. 1.

All these runs were made using the quinine sulfate filter, which cuts off all wave lengths shorter than 4050 Å. Another run was made using a piece of Corex Red Purple glass as a filter. This transmits the ultraviolet and also some light between 4000 and 4500 Å. The reaction occurred at a measurable rate, although it was somewhat slower than that with the

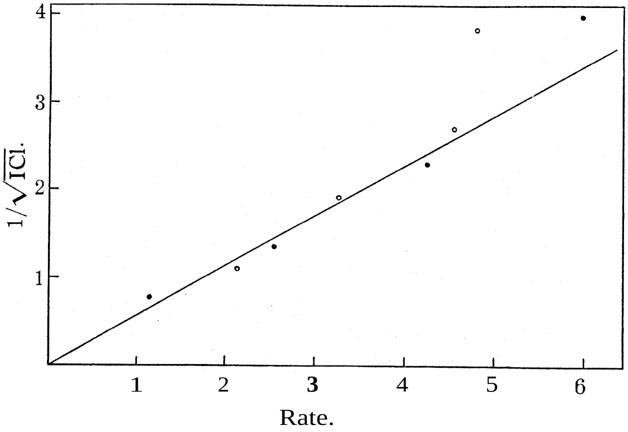

Fig. 2.

quinine sulfate filter, as might be expected due to lower intensity of the light source in the ultraviolet. Another run was made using a Wallace filter No. 8 which transmits between 4300 and 5600 Å.,[8] but in this ease no reaction was observed, even with long exposures, although the light absorbed by the iodine chloride in this case was greater than that absorbed by the chlorine in the test with the Corex filter.

Discussion of Results

From the experiments which have just been described we can conclude that it is not possible to bring about the formation of hydrochloric acid by the optical dissociation of iodine monochloride in hydrogen, either in the presence or absence of chlorine molecules. Furthermore, if we have a mixture of the three substances and illuminate with light which is absorbed by chlorine, a reaction occurs, but at a much slower rate than if no iodine chloride is present. This may seem to be in direct contradiction to the results published by Padoa,[9] who reported that the formation of hydrochloric acid was accelerated by the addition of iodine. His experiments, however, were carried out using an actinometer in which water was present, and it is well known that under such circumstances the chlorine would oxidize the iodine to iodate, so it is very unlikely that he had any appreciable amount of any iodine compound in the gas phase.

Let us consider the first conclusion above from the standpoint of the two interpretations which have been given to the absorption spectrum of iodine chloride. If the interpretation given most recently by Gibson is correct, i. e., the molecule is dissociated into a normal iodine atom and an excited chlorine atom, it is difficult to see why we should fail to observe the formation of hydrochloric acid. Regardless of whether the chains in the hydrochloric acid reaction are started by normal or activated atoms under ordinary circumstances, if we introduce the atoms in the higher state, they must start a reaction either at once or as soon as they have been brought to the normal state, which would be a matter of frequent occurrence at the pressures used. On the other hand, if the original interpretation of Gibson and Ramsperger is correct, and normal atoms are formed in the optical dissociation of iodine chloride, the number of chlorine atoms in the first excited state, the $^2P_1$ state, would be very small, as the average kinetic energy of molecules at room temperature is not sufficient to cause any appreciable fraction of the atoms to be in the higher state. If, under such circumstances, the reaction with hydrogen requires the activated atom, then we should expect just what was actually observed, namely, no formation of hydrochloric acid. From the experiments which we have

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[8] The amount of reaction which would be caused under these conditions by the absorption of light in this region by the chlorine is negligible.

[9] Padoa, *Gazz. chim. ital.*, **51**, I, 193 (1921).

described it is, therefore, possible for us to conclude definitely, first, that visible light of wave lengths less than 5744 A. dissociates iodine chloride into two normal atoms; second, the reaction chains in the formation of hydrochloric acid are started by chlorine atoms in the $^2P_1$ state and not by the normal atoms. It remains undetermined whether or not the chain goes through a Cl_3 stage.

With regard to the inhibiting effect of iodine chloride on the reaction, it is much easier to give a qualitative picture than to account for the quantitative result. Among the more probable explanations would be the reduction of the concentration of chlorine atoms in the $^2P_1$ state due to collisions with iodine chloride being very efficient in bringing about a return to the normal state. Or we may have reactions such as

$$Cl^* + ICl = Cl_2 + I$$
$$H + ICl = HCl + I$$

Either of these would terminate the chain since the iodine atoms do not react with hydrogen. The iodine atoms would eventually be converted into iodine chloride. Such reactions would be expected to cause an inhibiting action proportional to the first power of the iodine chloride pressure, whereas the observed effect was definitely less. The explanation of the discrepancy is not apparent, but it may be that other apparatus which will be capable of studying the reaction over a wider range of conditions will be able to produce a key to the solution.

Summary

The photochemical formation of hydrochloric acid in the presence of iodine chloride has been studied at room temperature. From the experimental data obtained it has been shown that the following conclusions may be drawn.

1. Iodine chloride is dissociated into normal atoms by the action of light of wave length less than 5744 Å.
2. The formation of hydrochloric acid requires the presence of chlorine atoms in the $^2P_1$ state.
3. The rate of formation of hydrochloric acid by light of wave length greater than 4050 Å. is inversely proportional to the square root of the iodine chloride pressure.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

AZIDO-CARBONDISULFIDE. IV. PREPARATION AND PROPERTIES OF THE NEW INTER-HALOGENOID, CYANOGEN AZIDO-DITHIOCARBONATE[1,2]

BY L. F. AUDRIETH AND A. W. BROWNE

WITH MICROSCOPICAL STUDIES BY C. W. MASON

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Among the recent accessions to the list of halogen-halogenoids probably capable of existence are bromine azide,[3] thiocyanogen monochloride and trichloride,[4] chlorine azido-dithiocarbonate,[5] and the mono-bromine and tri-bromine azido-dithiocarbonates.[5] A new method for the preparation of cyanogen selenocyanate, a substance included within the smaller group of inter-halogenoids, has been described.[6]

The somewhat wide-spread attention devoted at present to compounds of this type finds justification not merely in the inherent scientific interest to be found in each of these substances, but also in the contribution made by each of them to the gradually extending chemical series of electronegative substances comprising both the halogens and the halogenoids or "pseudo-halogen^."^ The present article deals with the formation, preparation, properties and behavior of a new inter-halogenoid, cyanogen azido-dithiocarbonate.

Formation and Preparation.—Cyanogen azido-dithiocarbonate is formed under appropriate conditions by interaction either of negative cyanide and positive azido-dithiocarbonate radicals, or of positive cyanide and negative azido-dithiocarbonate radicals.

Mercuric cyanide, for example, either in the solid state or in aqueous solution, reacts with azido-carbondisulfide in ether, alcohol or acetone in accordance with the equation

$$Hg(CN)_2 + 2(SCSN_3)_2 = Hg(SCSN_3)_2 + 2CN{\cdot}SCSN_3 \qquad (1)$$

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[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. It was presented at the Detroit Meeting of the American Chemical Society, in September, 1927. The present paper is Article 6 under Heckscher Grant No. 60. For Articles 1, 2, 3, 4 and 5 see (a) THIS JOURNAL, 45, 2604 (1923); (b) 47, 1916; (c) 2698 (1925); (d) 49, 2129 (1927); (e) 52, 1928 (1930) For Articles 1, 2, 3 and 4 under Heckscher Grant No. 4, see (f) *ibid.*, 44, 2106; (g) 2116; (h) 2315 (1922); (i) 45, 2541 (1923).

[2] Manuscript received April 11, 1929

[3] Spencer, *J. Chem. Soc.*, 127, 216 (1925).

[4] Kaufmann and Liepe, *Ber.*, 57, 923 (1924); Lecher and Joseph, *ibid.*, 59, 2603 (1926).

[5] Gardner and Browne, THIS JOURNAL, 49, 2759 (1927).

[6] Kaufmann and Kogler, *Ber.*, 59, 178 (1926). See also Verneuil, Ann. *chim. phys*, [6] 9, 326 (1886).

[7] Birckenbach and Kellermann, *Ber.*, 58, 786, 2377 (1925).

Three grams of slightly moist azido-carbondisulfide, prepared by the method of Erowne, Hoel, Smith and Swezey,[1i] was dissolved in acetone and 1.8 g. of finely powdered mercuric cyanide was added to the solution. After prolonged agitation of the reacting mixture, pearly flakes[8] of mercuric azidodithiocarbonate, found under the microscope to consist of thin, hexagonal plates, were precipitated. The solid was removed by filtration, the filtrate evaporated to dryness and the residue extracted with ether. The extract yielded, on evaporation, a white solid identical in crystallographic and chemical properties with cyanogen azido-dithiocarbonate as prepared by the second method. The difficulty of obtaining the product free from traces of mercury, and the smallness of the yields produced have led to the choice of the alternative method.

To 50 cc. of a cold aqueous solution that contained about 3 g. of sodium azido-dithiocarbonate was added 2.4 g. of freshly prepared cyanogen bromide dissolved in 20 cc. of ether. After the reacting mixture, cooled in the ice-bath, had been shaken for a few minutes, a finely crystalline solid appeared in the aqueous layer. This was filtered on a Buchner funnel, washed with cold water and partially dried by suction. Desiccation was completed over phosphorus pentoxide in the ice chest. The yield of cyanogen azido-dithiocarbonate amounted to about 85% of the theoretical, calculated on the basis of the equation[9]

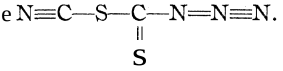
$$CNBr + KSCSN_3 = KBr + CN{\cdot}SCSN_3 \qquad (2)$$

Analysis.—Sulfur was determined by oxidizing the substance with sodium peroxide in the Parr bomb and weighing the sulfur as barium sulfate. Nitrogen was determined by the Dumas method as modified in this Laboratory for use in analyzing potassium azido-dithiocarbonate.[1h]

Anal. (a) Subs., 0.1055, 0.1307: $BaSO_4$, 0.3410, 0.4225. Calcd. for $CN{\cdot}SCSN_3$: S, 44.47. Found: S, 44.39, 44.40. (b) Subs., 0.1914, 0.1778: N_2, 59.96 cc. (0.0751 g.), 55.23 cc. (0.0692 g.). Calcd. for $CN{\cdot}SCSN_3$: N, 38.87. Found: N, 38.86, 39.19.

Determinations of the molecular weight in benzene were made by the cryoscopic method. Subs., 0.4042, 0.5015, 0.4560: solvent, 26.87, 23.73, 17.58; AT, 0.535°, 0.810°, 0.929". Calcd. for $CN{\cdot}SCSN_3$: mol. wt., 144. Found: 144, 130, 140.

On the basis of these results, cyanogen azido-dithiocarbonate is believed to possess the structure



$$N{\equiv}C{-}S{-}\underset{\underset{\displaystyle S}{\|}}{C}{-}N{=}N{\equiv}N.$$

Properties.—Cyanogen azido-dithiocarbonate is a white, crystalline solid, soluble in water at 0° to the extent of about 1.5 g. per liter, and more soluble in various organic

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[8] The precipitate was identified, by an extended series of qualitative tests, with mercuric azido-dithiocarbonate, a very explosive compound which, with various other heavy metal salts of azido-dithiocarbonic acid, has been isolated, analyzed and studied in this Laboratory.

[9] The use of cyanogen bromide in this reaction, and in the preparation of cyanazide [(a) Darzens, *Compt. rend.*, 154, 1232 (1912)], suggests the general applicability of this reagent in the formation of other interhalogenoids. It has been found in this Laboratory that cyanogen thiocyanate (sulfur dicyanide), for example, may be formed by the interaction of an ethereal solution of cyanogen bromide and an aqueous solution of potassium thiocyanate, as expressed by the equation $CNBr + KSCN = CN{\cdot}SCN + KBr$. This interhalogenoid, which has been prepared previously by other methods [(b) Linnemann, *Ann.*, **120**, 36 (1861); (c) Svderback, *ibid.*, **419**, 217 (1919); (d) Schneider, *J. prakt.* Chem., [2] **32**, 187 (1885)] was obtained in relatively small yields in the form of a crystalline substance which melts at 62°, volatilizes readily and possesses the overpowering odor characteristic of the cyanogen halides.

solvents. It is distinctly less unstable than azido-carbondisulfide,[11] and unlike this substance is insensitive to mechanical impact.

When prepared by the second method, the substance possesses a barely perceptible odor, suggesting that of cyanogen and the cyanides. In finely divided form the solid has a decided sternutatory effect. If prepared in contact with organic solvents, many of which tend to catalyze its decomposition, it has a more pronounced odor, somewhat resembling that of cyanogen iodide, and undoubtedly due to the presence of cyanogen thiocyanate, the principal product of its decomposition.

In the Bunsen flame small samples of the interhalogenoid decompose with a scarcely audible puff, and a violet flash. When heated in a somewhat restricted space, as in an open test-tube, larger quantities invariably explode with a fairly sharp detonation at 65–70°. An interesting sequel to each of these explosions was the liberation of a heavy, dark orange vapor, of an odor comparable with that of thiocyanogen and also with that of cyanogen thiocyanate. Very small samples heated in the Thiele melting-point tube withstand somewhat higher temperatures. At 60° the samples assume a yellowish tint, which deepens with rising temperature, until at 80.5–81° fusion takes place with decomposition and formation of a yellowish-orange (YO-0 on the Milton Bradley Standard)[10] residue.

Cyanogen azido-dithiocarbonate undergoes gradual spontaneous decomposition at room temperatures, with liberation of nitrogen and formation of a solid residue probably consisting of a mixture of free sulfur, polymerized thiocyanogen and cyanogen thiocyanate. This decomposition, which undoubtedly involves initial evolution of nitrogen, is believed to proceed subsequently in two different directions: (1) liberation of sulfur and formation of cyanogen thiocyanate, as expressed in Equation 3, and (2) liberation of thiocyanogen, in accordance with Equation 5. Both the cyanogen thiocyanate and the thiocyanogen evidently polymerize, as indicated in Equations 4 and 6.

$$\mathrm{CN{\cdot}SCSN_3} = \mathrm{N_2} + \mathrm{S} + \mathrm{CN{\cdot}SCN} \qquad (3)$$
$$x\mathrm{CN{\cdot}SCN} = (\mathrm{CN{\cdot}SCN})_x \qquad (4)$$
$$\mathrm{CN{\cdot}SCSN_3} = \mathrm{N_2} + 2\mathrm{SCN} \qquad (5)$$
$$x\mathrm{SCN} = (\mathrm{SCN})_x \qquad (6)$$

The formation of a volatile product containing the thiocyanogen group was demonstrated by allowing a current of dry air that had passed over the solid to impinge upon filter paper moistened with ferric chloride solution. The characteristic red coloration soon appeared. The composition of the solid residue was determined by extraction with carbon disulfide, over a period of 150 hours, which accomplished complete removal of free sulfur, and analysis of the remaining solid, which was found to be intermediate in composition between thiocyanogen and cyanogen thiocyanate.

The velocity of decomposition of the interhalogenoid was measured in a series of nitrometric determinations conducted at room temperature (22.7"). In a typical experiment, of which the results are presented graphically in Fig. 1, a sample of cyanogen azido-dithiocarbonate weighing 0.3203 g. was placed in the nitrometer bulb. The volume of nitrogen liberated was read every twelve hours over a period of 1100 hours, during which a total of 51.7 cc. (corr.), corresponding to 1.016 mol of nitrogen per mol of the solid was evolved.

As the temperature is raised the velocity of decomposition undergoes marked acceleration. At 40°, for example, complete decomposition takes place within eighty hours. In a typical experiment 0.5433 g. of the original solid yielded 86 cc. (corr.), or 1.019 mol of nitrogen. The results are depicted in Fig. 2.

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[10] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1st ed., 1905, Vol. I, p. 232.

The concavity shown by the lower part of each curve toward the axis of ordinates indicates that the reaction is autocatalytic, and is therefore similar in type to the decomposition of azido-carbondisulfide.[1]

Pure white cyanogen azido-dithiocarbonate, after standing at room temperature for eighteen hours, takes on a light yellow color (YT2–YT1). After forty hours it assumes a very light orange-yellow tint (YT1–OYT2) and after forty-eight hours it attains its final color (Y–OY), which is intermediate between yellow and orange-yellow.[10]

Under the microscope the freshly prepared crystals are observed to consist of fine needles and thin prisms. These show parallel extinction and negative elongation, with fairly strong birefringence. The index of refraction for vibrations parallel to the long direction is 1.490; for vibrations transverse, between 1.7 and 1.8.

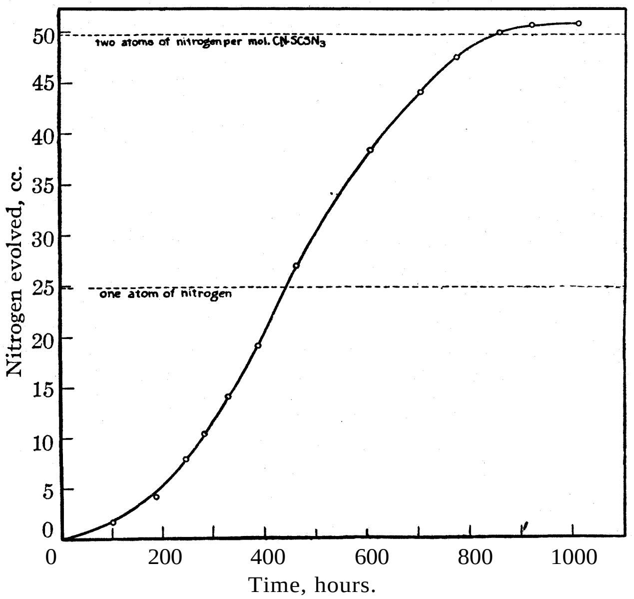

Fig. 1.—Nitrometric decomposition of cyanogen azido-dithiocarbonate at 22.7°.

The substance crystallizes from xylene or benzene in prisms which are laterally elongated rhombic bipyramids, and in rhombs which correspond to the unit prism, basal pinacoid and macradome. These have acute angles of about 62°, and show symmetrical extinction. They are biaxial, negative, with 2V fairly large. The axial plane bisects the acute angle of the rhombs. The prisms show a very well-defined basal cleavage. The general habit of both prisms and rhombs is similar to that of ammonium perchlorate. The symmetry and the optical tests indicate tbat the crystals belong to the orthorhombic system.

On recrystallization from benzene the crystals "sweat" a yellow oil which is apparently insoluble in benzene. When touched with a hot wire under the microscope the crystals melt and evolve gas copiously. The melt is yellow and on cooling behaves as a supercooled liquid. Seeded with cyanogen azido-dithiocarbonate it solidifies almost completely, with a small amount of yellow oily material surrounding the crystals. The melt contains varying amounts of a brown, amorphous, isotropic, flocculent material, which does not appear to be a product of the decomposition at room temperature.

Solubility.—The solubility of cyanogen azido-dithiocarbonate at 0° in various non-aqueous solvents was determined by cooling solutions saturated at room temperatures in the ice-bath. After crystallization had occurred, 5-cc. samples of the supernatant liquid were in each case pipetted into weighed containers and the solvent was removed by evaporation. The results are presented in Table I.

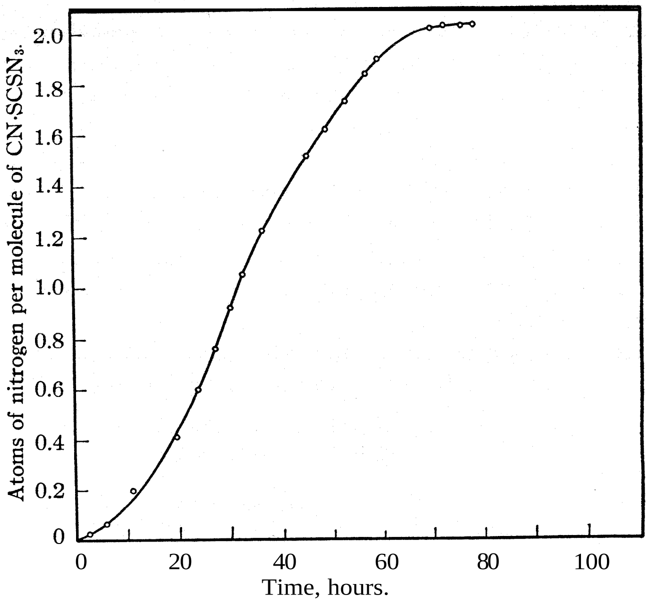

Fig. 2.—Nitrometric decomposition of cyanogen azido-dithiocarbonate at 40°.

TABLE I

SOLUBILITY OR $CN\cdot SCSN_3$ IN VARIOUS SOLVENTS

Solvent	*G.* of solid per 100-cc. solution
Acetone	24.69
Ethyl acetate	13.19
Methanol	6.27
Chloroform	3.17
Ethanol	2.61
Ether	1.11
Carbon disulfide	0.29
Carbon tetrachloride	0.22
Water	0.15

All organic solvents tend to accelerate the decomposition of cyanogen azido-dithiocarbonate. For this reason the use of such solvents in the purification of the interhalogenoid is precluded. In chloroform and benzene solutions, for example, complete decomposition with formation of an orange-yellow (OY-O) solid takes place at room temperature in twelve hours. At 50° a copious evolution of gas begins at once and the solid product appears in about fifteen minutes, while the solvent retains a part of the cyanogen thiocyanate in solution:

Behavior toward Alkalies.—Cyanogen azido-dithiocarbonate dissolves readily and completely in aqueous solutions of sodium or potassium hydroxide, yielding a light greenish-yellow (GYT2–GY) solution. Immediate neutralization of such solutions at 0° with dilute acids results in a re-precipitation of part of the interhalogenoid. The presence of cyanide, thiocyanate, sulfate and azido-dithiocarbonate ions in the residual solution was demonstrated by appropriate tests. After a short time interval the formation of sulfide, sulfite, thiosulfate and ammonium ions was found to have occurred at room temperature. Nitrogen and carbon dioxide were evolved.

Hydrolysis of cyanogen azido-dithiocarbonate may be considered to proceed in accordance with either Equation 7 or Equation 8.

$$CN{\cdot}SCSN_3 + 2KOH = KSCSN_3 + KOCN + H_2O \qquad (7)$$

$$CN{\cdot}SCSN_3 + 2KOH = KCN + KOSCSN_3 + H_2O \qquad (8)$$

The potassium azido-oxydithiocarbonate probably decomposes, with formation of the chlorate analog of azido-carbondisulfide, as described in an earlier article." This in turn undergoes decomposition, yielding a variety of products.

An entirely similar hydrolysis of the interhalogenoid is effected more slowly by water in the absence of alkalies. The products formed comprise the various free acids, in place of the metallic salts yielded by hydrolysis in alkaline solution. A yellow solid, consisting chiefly of dithiocyanic acid and free sulfur is gradually deposited from the solution.

Ammonolysis.—When a current of ammonia gas is caused to impinge upon dry cyanogen azido-dithiocarbonate, explosive decomposition of the solid ensues at once. Bubbled through an ethereal solution of the interhalogenoid, ammonia precipitates a white solid consisting chiefly of ammonium azido-dithiocarbonate, contaminated with some ammonium thiocyanate. On evaporating the ethereal solution to dryness, a sticky, orange-colored residue was obtained, of which the aqueous extract was found to contain cyanamide. It is therefore highly probable that ammonolysis proceeds in accordance with the equation

$$CN{\cdot}SCSN_3 + 2NH_3 = NH_4SCSN_3 + NH_2CN \qquad (9)$$

Behavior toward Acids.—Cyanogen azido-dithiocarbonate dissolves completely, with decomposition accompanied by evolution of gas, in concentrated sulfuric, hydrochloric or nitric acid. In the case of sulfuric acid the reaction takes place with almost explosive violence. With hydrochloric acid the resulting solution, at first clear and colorless, ultimately grows turbid owing to the separation of free sulfur. Treated with potassium iodide, the solution liberates iodine, indicating the presence of free chlorine, thiocyanogen or one of the various possible halogen-halogenoid or interhalogenoid compounds. Dilute mineral acids react more slowly than the concentrated acids, but eventually effect complete solution of the interhalogenoid. Glacial acetic acid behaves like the dilute mineral acids except that a yellow-orange (Y–YO) solid is finally deposited.

Miscellaneous Reactions.—Cyanogen azido-dithiocarbonate slowly reduces potassium permanganate in dilute acid and neutral solutions. It does not react with potassium bromate. It is oxidized at least partially by hydrogen peroxide in alkaline solution, with formation of sulfate ion. It dissolves in stannous chloride solution with evolution of gas and formation of a light yellow (YT2–YT1) solution. It dissolves slowly in dilute solutions of hydrazine hydrate and reacts violently with concentrated solutions, yielding hydrogen sulfide and free thiocyanogen. It liberates iodine from solutions of potassium iodide in the presence of concentrated hydrochloric acid.

It is soluble in aqueous solutions of potassium azido-dithiocarbonate, with probable initial formation of a *polyhalogenoid* such as $KSCSN_3\cdot CNSCSN_3$ or $KCN\cdot(SCSN_3)_2$, corresponding to the well-known polyhalides. The resulting solution smells strongly of cyanide, and after a time deposits solid azido-carbondisulfide

$$KSCSN_3 + CN\cdot SCSN_3 = KCN\cdot(SCSN_3)_2 \qquad (10)$$

$$KCN\cdot(SCSN_3)_2 = KCN + (SCSN_3)_2 \qquad (11)$$

Summary

Cyanogen azido-dithiocarbonate, $CNSCSN_3$, a new interhalogenoid, is formed by the interaction of azido-carbondisulfide and mercuric cyanide in acetone, but is best prepared by bringing together a cold, aqueous solution of sodium azido-dithiocarbonate and an ethereal solution of cyanogen bromide. It is a white, crystalline solid, slightly soluble in water, and more readily soluble in various non-aqueous liquids, especially acetone and ethyl acetate. It is stable at 0°, but undergoes a slow autocatalytic decomposition at room temperature, yielding thiocyanogen, cyanogen thiocyanate, sulfur and nitrogen.

The behavior of the interhalogenoid toward acids and alkalies, toward ammonia, and toward certain oxidizing and reducing agents has been studied.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

AZIDO-DITHIOCARBONIC ACID.
VI. SALTS OF COPPER, SILVER, GOLD, ZINC, CADMIUM, MERCURY, THALLIUM, LEAD AND BISMUTH[1,2]

BY G. B. L. SMITH, PAUL WARTTMAN AND A. W. BROWNE

WITH MICROSCOPICAL STUDIES BY C. W. MASON

RECEIVED JUNE 16, 1930 PUBLISHED JULY 3, 1930

One of the outstanding characteristics of azido-dithiocarbonic acid and its derivatives thus far described is the relative ease with which these substances undergo spontaneous thermal decomposition into nitrogen, sulfur and thiocyanic acid or its corresponding derivatives. In some instances the time required for complete decomposition of the substance at ordinary temperatures is but a few hours; in others it is a number of months. Exposure to light appears in certain cases to be an important, if not indeed a controlling factor. In other cases the influence of light seems to be practically negligible.

The sensitivity of the various azido-dithiocarbonates to mechanical impact also varies over a wide range. The ammonium and tetramethylammonium[2d] salts, for example, do not explode when struck with a hammer; the zinc, bismuth and anhydrous cadmium salts (*vide infra*), on the other hand, detonate, even under water, when subjected to very slight mechanical disturbance. This sensitivity, of the heavy metal azido-dithiocarbonates in particular, may reasonably lead to the expectation that certain of these compounds, suitably stabilized and partially desensitized, should prove to be useful as primers or detonators. In this event the coexistence of the brisant N_3 radical and inflammable atoms in the same molecule should offer an advantage over certain primers of the older type that is reminiscent of the superiority of the modern propellant or high explosive over ordinary black gunpowder. On the theory that the azido-dithiocarbonate radical may in a sense be regarded "as a labile combination of thiocyanogen with [molecular] nitrogen and sulfur,"[2a] the use of lead azido-dithiocarbonate, for example, as a constituent of a primer would be equivalent to the addition of one molecule of nitrogen and one atom of

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[1] For the earlier articles of this series see (a) THIS JOURNAL, **45**, 2604 (1923); (b) **47**, 2698 (1925); (c) **49**, 917 (1927); (d) 49, 2129 (1927); (e) 52, 1928 (1930). Manuscript received July 26, 1929.

[2] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present paper, which was presented orally and in abstract at the Ithaca meeting of the American Chemical Society in September, 1924, is Article No. 5 under Heckscher Grant No. 60. For articles 1 to 4 see Ref. 1, and also (a) THIS JOURNAL, **47**, 1916 (1925). For other literature related to the subject, and published from this Laboratory, see (b) *ibid.*, **44**, 2106 (1922); (c) **44**, 2315 (1922); (d) **44**, 2849 (1922); (e) 45, 2541 (1923); (f) **48**, 2383 (1926); (g) **49**, 2759 (1927).

sulfur to each molecule of lead thiocyanate, a substance that has already found use in this field.

The heavy metal azido-dithiocarbonates were considered by Sommer[3] to be of such enormously explosive character as to render inadvisable any closer investigation. To the authors of the present paper it has nevertheless seemed desirable, and entirely within the range of experimental feasibility, to isolate and describe certain of the typical heavy metal salts, as a preliminary to a more extended study of their explosive character.

In the present article are recorded the results obtained (a) in the preparation and investigation of six new compounds: $AgSCSN_3$, $Cd(SCSN_3)_2\cdot 2H_2O$, $HgSCSN_3$, $Hg(SCSN_3)_2$, $TlSCSN_3$, and $Pb(SCSN_3)_2$; (b) in the qualitative study of the azido-dithiocarbonates of copper, gold, zinc and bismuth, for none of which satisfactory quantitative data were obtained.

Preparation.—The heavy metal salts were prepared by interaction of aqueous solutions containing the azido-dithiocarbonate ion and aqueous solutions containing the respective metallic ion. The freshly prepared free acid[1a] was used as the source of the azido-dithiocarbonate ions, in place of the sodium salt employed by Sommer,[3] since the latter substance has been found more difficult to prepare relatively free from thiocyanate ion. In Table I are presented the analytical data for the compounds isolated.

TABLE I

ANALYTICAL DATA POR HEAVY METAL AZIDO-DITHIOCARBONATES

Formula		Analyses, % Calrd	Found	Constituent weighed as
$AgSCSN_3$	Ag	47 73	47 56, 47 51	AgCl
	$SCSN_3$	52 27	52 64, 53 06	$HSCSN_3$
$Cd(SCSN_3)_2\ 2H_2O$	Cd	29 22	29 58, 29 50	CdS
	S	33 34	33 24, 33 28	$BaSO_4$
$HgSCSN_3$	Hg	62 93	63 16, 67 76	HgS
	S	20 12	20 45, 20 23	$BaSO_4$
$Hg(SCSN_3)_2$	Hg	45 96	46 09, 46 01	HgS
	S	29 35	29 41, 29 50	$BaSO_4$
$TlSCSN_3$	Tl	63 32	63 13, 63 28	Tl_2PtCl_6
	S	19 90	19 86, 20 02	$BaSO_4$
$Pb(SCSN_3)_2$	Pb	46 72	46 60, 46 61	$PbSO_4$
	S	28 93	29 03, 28 99	$PbSO_4$

Properties of the Heavy Metal **Azido-dithiocarbonates.**—All of the compounds studied are insoluble in water in the ordinary sense of the term. The very low concentration of azido-dithiocarbonate ion present in the filtrate from an aqueous suspension of any of these substances is sufficient,

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[3] Sommer, Ber., 48, 1833 (1915); "Die diesbezüglichen Versuche wurden nur qualitativ ausgefuhrt und auf die Isolierung der reinen Verbindungen Verzicht geleistet, da der enorm explosive Charakter fast aller Schwermetallsalze eine nähere Untersuchung nicht ratsam erscheinen liess."

however, to permit catalysis of the reaction between iodine and potassium trinitride.[2b]

The azido-dithiocarbonates of copper, silver and univalent mercury are obtained in the form of flocculent precipitates. The azido salts of the other heavy metals, with the exception of gold, are precipitated in distinctive crystalline form. All of the salts, except that of gold which decomposed thermally during the process of drying at room temperature, were found to be sensitive to mechanical shock. Those of copper, silver, mercury (ous and ic), cadmium (hydrated), thallium and lead are obtainable in the dry state without serious hazard, but detonate violently under rather slight mechanical provocation. Those of zinc and bismuth detonate at ordinary temperatures under water during the process of crystallization. From the numerous qualitative observations made it appears that the sensitivity to mechanical impact of compounds of heavy metals in the first and second groups of the periodic system varies inversely, while the brisance of the explosion varies directly with the atomic weight. On the other hand, the sensitivity of compounds of metals in the series mercury to bismuth varies directly and the brisance inversely with the atomic weight.

The behavior of the compounds toward various reagents and solvents is indicated in Table II.

TABLE II

BEHAVIOR OF THE HEAVY METAL AZIDO-DITHIOCARBONATES TOWARD SOLVENTS AND REAGENTS

Legend: D, detonated; V, very soluble, or vigorously attacked; M, moderately soluble, or moderately attacked; S, slightly soluble, or but little attacked; I, insoluble, or unattacked

	C_2H_5OH	CH_3OH	CCl_4	CS_2	$(C_2H_5)_2O$	C_6H_6	$(CH_3)_2CO$	Concd. H_2SO_4	1:6 H_2SO_4	Concd. HNO_3	1:6 HNO_3	Concd. HCl	1:6 HCl	Glacial $HC_2H_3O_2$	1:6 $HC_2H_3O_2$	NH_4OH soln.	NaOH soln.
$AgSCSN_3$	I	I	I	I	I	I	I	V	I	S	I	S	I	I	I	S	S
$Cd(SCSN_3)_2 \cdot 2H_2O$	M	M	I		M	I		D	M	M	M	M	M	S	M		
$HgSCSN_3$	I	I	I	I	I	I	I	D	I	M	I	S	I	I	I	M[a]	M[n]
$Hg(SCSN_3)_2$	I[a]	I[a]	I	I	I	I	I[a]	D	I	S	I	S	S	I	I	I[a]	I[a]
$TlSCSN_3$	I	S	I	I	I	I	I	D	M	M	M	M	S	I	S	S[a]	S[a]
$Pb(SCSN_3)_2$	I	I	I	I	I	I	I	V	V	V	M	V	V			S	S
Cu **salt**								V	M	M	M	S				S	S

[a] Darkened, probably as the result of photochemical action.

Copper Azido-dithiocarbonate.—This salt is yellow (Y) when moist, and dark yellow (YS1) in the solid state. Numerous unsuccessful attempts to obtain a copper compound of uniform[4] composition indicate that cupric ion interacts with azido-dithiocarbonate ion to form a mixture of cuprous and cupric azido-dithiocarbonates, which undergoes slow thermal decomposition with formation of an inert product, probably consisting of the copper thiocyanates.

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[4] **Mulliken**, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1905, Vol. I, 1st ed., p. **232**,

Silver Azido-dithiocarbonate, $AgSCSN_3$.—This white slightly photosensitive compound, either in aqueous suspension or in the solid state, tends to darken on exposure to light. It is soluble in pyridine, and may be recrystallized from this solvent in rosets of needle crystals.

Gold Azido-dithiocarbonate.—Auric and azido-dithiocarbonate ions interact in aqueous solution with initial precipitation of azido-carbondisulfide, accompanied by discharge of the yellow color. After one hour a bulky, white, fibrous precipitate fills the entire solution. After sixteen hours this precipitate assumes a dark orange-yellow color (OYS1). Under the microscope it appears as strikingly distorted crystals that grow as bunches of long fibers having the appearance of vegetable fibers. They are anisotropic and show parallel extinction. Characteristic crystals of azido-carbondisulfide may be seen. The solid is in all probability a mixture of aurous azido-dithiocarbonate and azido-carbondisulfide formed in accordance with the equation

$$Au^{+++} + 3SCSN_3^- = AuSCSN_3 + (SCSN_3)_2$$

Zinc Azido-dithiocarbonate.—After a delay of a few minutes, characteristic of all heavy metal azido salts of this group, a beautifully crystalline precipitate, composed of easily visible regular octahedra, is formed. Various attempts to separate this precipitate from the mother liquor have resulted in explosions, owing to the great sensitivity of the zinc azido salt. Immersion of samples of metallic zinc in an aqueous solution of the free azido acid results in the incrustation of the metal with a yellow solid exceedingly sensitive to friction.

Cadmium Azido-dithiocarbonate Dihydrate, $Cd(SCSN_3)_2 \cdot 2H_2O$.—Several subaqueous detonations of this salt have been observed. These may be attributable to initial formation of the very sensitive anhydrous salt which, if it escaped detonation, should subsequently undergo hydration. The dihydrate undergoes slow, spontaneous, quantitative, thermal decomposition in accordance with the equation

$$Cd(SCSN_3)_2 \cdot 2H_2O = Cd(SCN)_2 + 2N_2 + 2S + 2H_2O$$

Under the microscope the dihydrate appears as long, fine needles with end faces not well formed, apparently oblique, prismatic, with indistinct cross sections. The crystals are strongly doubly refractive, and have a high index of refraction, which prevents sharp observation of the extinction angle. This probably has a maximum value of about 35°. Dispersed extinction appears to be exhibited, and is seen best with thin crystals giving low order polarization colors, which change but do not extinguish at any definite point.

Mercurous Azido-dithiocarbonate, $HgSCSN_3$.—This substance when first formed is of a dark brown color, but when stirred the suspended precipitate becomes white. Preliminary preparations were found by analysis to consist of a mixture of the mercurous salt and free mercury.

Mercuric Azido-dithiocarbonate, $Hg(SCSN_3)_2$.—An aqueous suspension of this substance shows something of the appearance of "watered silk." The salt undergoes spontaneous thermal decomposition at room temperature, yielding as a final product mercuric thiocyanate which when ignited gives the characteristic "Pharaoh's serpents."

Thallous Azido-dithiocarbonate, $TlSCSN_3$.—This is a very light yellow (YT2) crystalline solid which under the microscope appears as didendritic and skeletal forms of oblique formation. The prevailing angle between branches is about 45°. The forms exhibit oblique extinction, and show gray polarization colors, with some light yellow. The refractive index is fairly high. No clean-cut single forms are evident.

Lead Azido-dithiocarbonate, $Pb(SCSN_3)_2$.—This compound which was obtained in the form of a very light greenish-yellow (GYT2) crystalline solid was deemed sufficiently stable for use in the gravimetric determination of the azido-dithiocarbonate ion. Weighed samples of the sodium azido salt dihydrate were dissolved in 100 cc. of water, and treated with an excess of lead acetate in aqueous solution. The precipitate was filtered on a tared Gooch crucible, washed with water, alcohol and ether, dried over phosphoric anhydride and weighed.

Anal. Subs., 0.3920, 0.2417: $Pb(SCSN_3)_2$ obtained, 0.4916, 0.3026. $NaSCSN_3 \cdot 2H_2O$ found: 0.3927, 0.2418.

When precipitated directly on the microscope slide the lead azido salt at first appears as rosets of fine, highly birefringent needles, the tiniest of which show brilliant polarization colors. When formed more slowly, or when allowed to stand, the crystals assume the form of lath-shaped prisms, often turned in X's and rosets. Thickened crystals show yellow by transmitted light. Unit prism and basal pinacoid forms are seen. The forms with oblique ends show oblique extinction, the apparent extinction angle being about 19°. In oblique-ended forms the end angle in the plane of the prism face is about 68°. Forms showing pointed ends show parallel extinction. The crystals are in all probability monoclinic.

Bismuth **Azido-dithiocarbonate.**—This azido salt is obtained as a light yellow (YT1–YT2) precipitate when bismuth nitrate acidified with nitric acid interacts with the azido-acid in aqueous solution. During subsequent treatment with water the color deepens to a reddish-orange (RO). Under certain conditions the precipitate shows the deeper color at the outset. These precipitates are highly sensitive and have been observed to detonate under water.

Summary

Six heavy metal salts of azido-dithiocarbonic acid have been prepared and described: silver azido-dithiocarbonate, $AgSCSN_3$; cadmium azido-dithiocarbonate dihydrate, $Cd(SCSN_3)_2 \cdot 2H_2O$; mercurous azido-dithiocarbonate, $HgSCSN_3$; mercuric azido-dithiocarbonate, $Hg(SCSN_3)_2$; thallous azido-dithiocarbonate, $TlSCSN_3$; and lead azido-dithiocarbonate, $Pb(SCSN_3)_2$. Qualitative observations have been made upon the corresponding salts of copper, gold, zinc and bismuth.

Azido-dithiocarbonates of the heavy metals in the first and second groups of the periodic system show a sensitivity to mechanical impact that varies inversely, while the brisance of the explosion varies directly with the atomic weight. On the other hand, the sensitivity of compounds of metals in the series mercury to bismuth varies directly and the brisance inversely with the atomic weight.

ITHACA, NEW YORK

NOTES

A Convenient Form of Gas Combustion Pipet.—The following type of gas combustion pipet has been found convenient and possesses several advantages. There is absolutely no danger of leakage, the time necessary for a combustion is materially shortened, and the pipet is adaptable to various volumes of gas over a wide range. The apparatus is illustrated in the accompanying diagram. The main portion of the pipet consists of a piece of straight tubing of from 1 to 2 cm. diameter, and a length of 50 to 75 cm. A platinum wire having a diameter of about 0.15 mm. is sealed in at each end and runs axially through the tube. As in the ordinary form of pipet, the upper end is connected to a capillary tube and the lower end to a mercury reservoir. To prevent excessive heating due to the narrowness of the tube, the whole length is surrounded by an oil jacket having a diameter about 1 cm. greater than that of the tube.

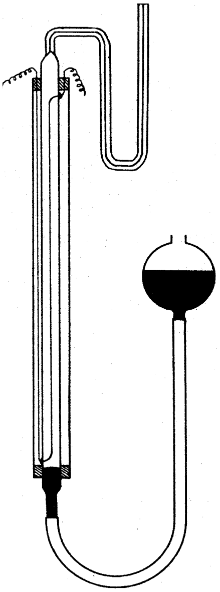
Fig. 1.

The pipet is extremely robust and no possibility of leakage exists. If desired it can also be used as an explosion pipet. On account of the axial situation of the filament the time necessary for a combustion is shortened to about two minutes. One great advantage of this form of pipet is its adaptability to different volumes of gas. For very small samples only a short length of the filament is exposed above the surface of the mercury. If the apparatus is used with 110 volts and an external resistance, the raising or lowering of the mercury level has practically no effect on the temperature of the wire. A similar type of pipet with a total volume of about 6 cc. has been found convenient with a "semi-micro" apparatus of the Ambler[1] type.

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The Temperature Coefficient of the Dielectric Constant of Water.—For the theoretical calculation of activity coefficients of strong electrolytes the dielectric constant of the medium, and not the less certain dD/dT, comes into question. The D of the pure solvent has in general been used, the justification of which is shown by Debye and Pauling.[1] Of

[1] H. R. Ambler, *Analyst*, **54**, 517 (1929).

[1] Debye and Pauling, THIS JOURNAL, **47**, 2129 (1925).

much greater importance in the theoretical treatment of integral heats of dilution is an exact knowledge of $\mathrm{d}D/\mathrm{d}T$. The more exact development of the fundamental theory of Debye and Hückel[2] by Gronwall, LaMer and Sandved[3] and the application of their calculations to the theoretical integral heats of dilution by Lange and Meixner[4] give $V_c = -\frac{N}{n}\sum_{j=1}^{s} n_j \frac{z_j\epsilon}{Da_j}\left[\psi_j - \frac{z_j\epsilon}{Da_j}\right]\left[1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}\right]$ ergs per mole of salt. The integral heat of dilution is equal to the ionic electrical potential energy at the concentration c less that at infinite dilution multiplied by the factor $\left[1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}\right]$, which is characteristic of the solvent alone. The numerical value of this factor is greatly influenced by small changes in $\mathrm{d}D/\mathrm{d}T$. The previous measurements of D and $\mathrm{d}D/\mathrm{d}T$ by Drude[5] and Kockel[6] show relatively large differences, as a result of which the theoretical V_c values at 25° show an uncertainty of approximately ±35%. Until now the value —0.337 for $\mathrm{d}D/\mathrm{d}T$ at 25° derived from the Drude interpolation formula $D = 88.23 - 0.4044t + 0.00135t^2$ has seemed most probable, as numerous measurements of the heats of dilution of 1–1 type salts in the concentration range $10^{-1} - 10^{-4}$ M made in this Laboratory show, within the limits of the experimental error, a proportionality of V_c with $\sqrt{c}$ below 0.0025 M and permit a rather certain extrapolation to $c = 0$, from which values of the initial slopes (A) are obtained ($V_c = A\sqrt{c}$) ranging from 290 to 430, that is, corresponding to "a" values of 1.25 to 5 A.

Within the past few months three new series of measurements of D for water have appeared.[7] For comparison of the various measurements, the accompanying table is given, and the various measurements are, for the sake of brevity, denoted by Drude (graphic) I, Drude (interpolated) II, Kockel III, Cuthertson and Maass IV, Drake, Pierce, and Dow V,

		12.5°			25°			40°	
	D	$\frac{\mathrm{d}D}{\mathrm{d}T}$	$1+\frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}$	D	$\frac{\mathrm{d}D}{\mathrm{d}T}$	$1+\frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}$	D	$\frac{\mathrm{d}D}{\mathrm{d}T}$	$1+\frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}$
I	82.77	−0.368	−0.269	78.26	−0.349	−0.329	73.18	−0.330	−0.411
II	83.39	− .371	− .269	78.96	− .337	− .272	74.21	− ,296	− .248
III	82.81	− ,404	− ,393	77.84	− ,385	− ,474	72.24	− ,349	− .512
IV	79.42	− .368	− .323	75.40	− .289	− .142	71.48	− .248	− .086
V	83.29	− .393	− .427	78.57	− .362	− .374	73.41	− .326	− .390
VI	83.16	− .379	− .376	78.54	− .361	− .371	73.28	− .341	− .457

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[2] Debye and Hiickel, *Pkysik. Z.*, 24, 193 (1923).

[3] Gronwall, LaMer and Sandved, *ibid.*, 29, 358 (1928).

[4] Lange and Meixner, *ibid.*, **30**, 670 (1929).

[5] Drude, *Wied. Ann.*, **59**, 48 (1896).

[6] Kockel, *Ann. Physik.* **77**, 430 (1925).

[7] Cuthbertson and Maass, THIS JOURNAL, **52**, 483 (1930); Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930); Wyman, *ibid.*, **35**, 623 (1930).

Wyman VI. It is readily seen that the theoretically important factor $\left[1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}\right]$ is extraordinarily sensitive to small differences in $\mathrm{d}D/\mathrm{d}T$. The good agreement of V and VI at 25° is fortuitous, as is seen from an examination of the various factors at other temperatures. III and IV must be regarded as incorrect not only because of poor agreement with the other measurements but also in view of the improbable value given for $\left[1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}\right]$, a value not easily reconciled with the experimental measurements of V_c. It would seem that the exact values of $\mathrm{d}D/\mathrm{d}T$ lie between those of measurements I, II and V, VI; at any rate it cannot be said, unfortunately, that we have obtained more probable values of these theoretically important factors in spite of the several comprehensive series of newer measurements. For a comparison of measured and calculated integral heats of dilution it is necessary that $\mathrm{d}D/\mathrm{d}T$ be known with an accuracy of $\pm 0.5\%$, an accuracy which has probably not yet been reached in these difficult measurements.[8]

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Inorganic Lubricants. II. Phosphoric Acid **Mixtures.**—The use of moistened phosphorus pentoxide, boiled orthophosphoric acid and similar materials as inorganic lubricants on glass stopcocks and ground connecting tubes has been more or less common practice[1] wherever organic lubricants must be avoided. Such materials, however, have the disadvantage of being markedly hygroscopic in moist air, and eventually become thin, watery and of lower lubricating value.

Stephens' recently described phosphoric acid mixture[2] is a lubricant of superior physical properties, but this product also is freely hygroscopic in air of moderate humidity.

Phosphoric acid mixtures containing chiefly metaphosphoric acid, on the other hand, are not markedly hygroscopic in air of even as high humidity as 80%, except after exposure of weeks or months, and then only slightly. The following procedure yields a satisfactory lubricant of this nature.

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[8] A more detailed discussion of these various series of dielectric constant measurements will be included in a paper to be read at the Heidelberg meeting of the Bunsen Society, May 29–31. The paper will be published in *Z. Elektrochem.*, *36*, (1930).

[1] See, for example, Baxter and Chapin, *Proc. Am. Acad. Arts Sci.*, *46*, 239 (1910); Richards and Krepelka, THIS JOURNAL, 42, 2256 (1920).

[2] Stephens, *ibid.*, 52, 635 (1930).

Dissolve 10 g. of metaphosphoric acid (glacial phosphoric acid in fused sticks) in 100 cc. of distilled water, add 2 g. of boric acid crystals and stir until dissolved. Evaporate this mixture on the steam-bath to about 25 cc. and add 1 cc. of 85% orthophosphoric acid. Boil gently and stir with a thermometer until the temperature reaches 122°. Cool somewhat and transfer to a bottle.

The product is a transparent, colorless, viscous sirup that, in addition to being reasonably stable in air, does not set or crystallize over a period of several months. Moreover, it is sufficiently thermoplastic to become markedly less viscous when heated gently. The boric acid appears to increase the viscosity somewhat and to aid in preventing crystallization. The viscosity can be further increased by boiling to a higher temperature.

A lubricant of similar properties containing chiefly water-soluble sodium metaphosphate may be prepared as follows.

Ten grams of the sodium metaphosphate (prepared by heating monosodium phosphate or sodium ammonium phosphate in platinum over a blast lamp until a quiet melt at redness is obtained) is dissolved in 50 cc. of distilled water. Two grams of borax is added and dissolved and the solution evaporated on the steam-bath to a volume of about 25 cc. and then boiled over a small free flame until the temperature reaches 106°. Such a mixture may become slightly cloudy on standing, but this does not appear to affect its usefulness.

These lubricants may be used with organic vapors and liquids, some acid vapors and with neutral gases, but crystallization may develop in the presence of alkaline vapors. There is little tendency to freeze or "grab." They have a low but definite aqueous vapor pressure and so may not be employed when water vapor must be strictly excluded.

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STUDIES IN THE DIARYL ACYL HYDRAZINE SERIES. I

BY JOHN J. RITTER AND FRANK O. RITTER

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The diaryl acyl hydrazines of the type $ArNCOCH_3NHAr$ have been hitherto little investigated. The only previously known members of this series are mono-acetylhydrazobenzene,[1] mono-acetylbenzene-hydrazo-*p*-toluene,[2] and mono-acetylhydrazo-*p*-toluene.[1]

The acetylation of aromatic hydrazo compounds, by means of which the members of this group may be prepared, was undertaken by us to gain some knowledge of the relative reactivities of the N atoms of the hydrazo linking in unsymmetrical members of the series, of the type Ar′NHNHAr. The behavior of hydrazo compounds on rearrangement in acid solution has been thoroughly investigated[3] with reference to the effect of the presence of the more common substituent groups in the aryl nuclei. The effect of such structural modifications upon the hydrazine residue, however, has not previously been studied; it has been found possible by us to detect such changes by treatment with acetic anhydride, which had previously been shown, in the cases cited above, to yield mono-acetyl derivatives readily. We have therefore prepared and studied several of the mono-acetyl derivatives of the unsymmetrical hydrazobenzenes from this point of view.

The structures of these compounds were determined by reduction with phenylhydrazine. The present paper describes the preparation and identification of these compounds; an alternative method of identification involving oxidation of the acetyl derivatives, with the description of some new members of this series, and the bearing of this research upon the rearrangement of hydrazo compounds in acid solution, will be presented in a later communication. Of the compounds described here it was found that each of the following yields two isomeric mono-acetyl derivatives in approximately equal amounts: benzene-hydrazo-p-toluene, *p*-chlorohydrazobenzene and p-bromohydrazobenzene. Benzene-hydrazo-o-toluene yields a single mono-acetyl derivative. It is of interest to note also that we have observed in this series the kind of isomerism shown by monobenzoylhydrazobenzene, and described by Freundler.[4] Mono-acetyl-*p*-bromohydrazobenzene was isolated in three forms, one of which changed gradually into one of the others during several weeks.

The reduction of the mono-acetylhydrazo compounds by phenylhydrazine severs the nitrogen atoms of the hydrazo linking, yielding the corre-

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[1] Stern, *Ber.*, 17, 380 *(1884);* Goldschmidt and Euler, *ibid.*, 55, 616 (1922).

[2] Jacobson and Lischke, *Ann.*, 303, 370 (1898).

[3] Jacobson, *ibid.*, 428, 90–99 (1922).

[4] Freundler, Compt. *rend.*, 136, 1554 (1903).

sponding amine and anilide. The reductiori products are easily separated by treatment with dilute acetic acid, in which the amine dissolves while the amide remains undissolved. This reduction method has been applied successfully to the mono-acetyl derivatives of hydrazobenzene and benzene-hydrazo-o-toluene, and to one of each of the two isomeric mono-acetyl derivatives of benzene-hydrazo-p-toluene, *p*-chlorohydrazobenzene and *p*-bromohydrazobenzene.

In our early experiments attempts were made to follow the reduction and judge of its completeness by measuring the volume of nitrogen evolved during the reaction, since phenylhydrazine on oxidation yields nitrogen as shown by the equation

$$C_6H_5NHNH_2 \longrightarrow C_6H_6 + N_2 + 2H$$

The volume of nitrogen evolved was in most cases less than the theoretical. Further addition of phenylhydrazine to the partly reduced acetylhydrazo compound resulted in the evolution of more nitrogen, even after an amount far in excess of the theoretical one mole had been added. Ammonia was also detected among the gaseous products of the reaction. These facts made it evident that the phenylhydrazine, in addition to its reaction with the acetylhydrazo compound, was undergoing self-oxidation–reduction

$$2C_6H_5NHNH_2 \longrightarrow C_6H_6 + N_2 + NH_3 + C_6H_5NH_2$$

Considering that phenylhydrazine boils at 242° with only slight decomposition, it seemed remarkable that decomposition should take place so readily at the temperature of these experiments (160–180°). In one experiment the rate of evolution of the nitrogen was measured and was found to increase rapidly for a time, as the reduction of the acetyl hydrazo compound progressed. It was evident that one of the reaction products catalyzed the self-oxidation–reduction of phenylhydrazine. A study of the behavior of phenylhydrazine at 160° in the presence of acetanilide and at 185° in the presence of acet-m-toluidide showed that both of these substances bring about rapid decomposition of the phenylhydrazine, while undergoing no change themselves. A similar effect has been reported by Just,[5] who observed that sulfanilic acid accelerated the self-oxidation–reduction of phenylhydrazine. A procedure, to be described in the experimental part, was finally developed whereby complete reduction of the hydrazo compound may be recognized.

For convenience in describing the acetylhydrazo compounds in the experimental part, the nitrogen atoms of the hydrazo linking will be designated as N and N', N referring to the nitrogen atom attached directly to the unsubstituted benzene nucleus.

Experimental Part

The unsymmetrical hydrazo compounds were prepared by reduction of the corre-

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[5] Just, *Ber.*, 19, 1207 (1886).

sponding azo compounds, the latter having been obtained by Wieland's[6] modification of Baeyer's[7] method. Treatment of the hydrazo compounds with acetic anhydride resulted in the mono-acetyl derivatives. The general procedures, which were substantially the same in all cases, will be briefly outlined

Preparation of the Azo Compounds.—Equimolar amounts of nitrosobenzene and the appropriate amine were condensed according to Wieland's procedure. In practically all cases nearly pure crystalline products were readily obtained in yields of about 80% of the theoretical: benzene-azo-p-toluene, m. p. 71–72", in agreement with Mills,* benzene-azo-o-toluene, b. p. 156–158° (corr.) at 4 mm. (Jacobson[g] reported this substance as a liquid at ordinary temperature) ; @-chloro-azobenzenem. p. 88°, in agreement with Heumann and Mentha;[10] *p*-**bromo-azobenzene,** m. p. 88°, in agreement with Jacobson and Grosse.[11]

Preparation of the Hydrazo Compounds.—The azo compounds were reduced with zinc dust and glacial acetic acid in boiling alcohol. This method was found to be more convenient than that of Jacobson and Lischke[2] in which reduction was accomplished with zinc dust and sodium hydroxide solution. The procedure in a typical experiment was as follows. Glacial acetic acid was added dropwise to a mixture of zinc dust and a 10–15% solution of the azo compound in boiling 95% alcohol until the solution became colorless. The solution was filtered hot and the filtrate cooled rapidly in an ice-bath. In some cases the hydrazo compound crystallized from the cold solution; in others, it was necessary to add ice water slowly to the alcoholic solution to bring about precipitation. The crystals were filtered and allowed to dry. The solvent evaporates rapidly from the crystalline products obtained in this way and the danger of air oxidation to the azo compound is thus greatly minimized. The products obtained by this procedure were colorless and apparently quite free from the azo compounds: **benzene-hydrazo-*p*-**toluene, m. p. 87–88' (Jacobson and Lischke[2] give 86–87"); benzene-hydrazo-o-toluene m. p. 101–102°, in agreement with Jacobson;[9] p-chlorohydrazobenzene, m. p. 90–91° (Heumann and Mentha[10] report 89–90°); p-bromohydrazobenzene, m. p. 115" in agreement with Janowsky and Erb.[12]

Acetylation of the Hydrazo Compounds.—The procedure described by Sternf[3] was employed. One part of the hydrazo compounds was dissolved in about three parts of freshly distilled acetic anhydride, and the mixture allowed to stand for several hours, usually overnight. The resulting solution was then added to about five parts of water and well shaken. The acetyl derivatives separated either as crystalline solids or as viscous oils which slowly solidified on standing. It was found that the structurally isomeric acetyl derivatives, when formed, could be separated by recrystallization from 95% alcohol. One of the isomers in each case was found to crystallize from the hot solution on cooling, while the second could be isolated by slow spontaneous evaporation of the mother liquor. As a class these compounds are colorless crystalline solids, rather soluble in alcohol, ether, chloroform and boiling benzene, and sparingly soluble in water and in ligroin

N'-Acetylbenzene-hydrazo-p-toluene, m. p. 140–141° (corr.) in agreement with Jacobson and Lischke.[2]

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[6] Wieland, *Ber.*, 48, 1107 (1915).

[7] Baeyer, *ibid.*, **7,** 1639 (1874).

[8] Mills, J. *Chem. Soc.*, 67, 930 (1895).

[9] Jacobson, *Ber.*, 28, 2544 (1895).

[10] Heumann and Mentha, *ibid.*, 19, 1687 (1886).

[11] Jacobson and Grosse, *Ann.*, **303,** 320 (1898).

[12] Janowsky and Erb, *Ber.*, 20, 358 (1887).

[13] Stern, *ibid.*, 17, 380 (1884).

N-Acetylbenzene-hydrazo-*p*-toluene, needles, m. p. 124°.

Anal. Calcd. for $C_{15}H_{16}ON_2$: N, 11.66. Found (micro-Dumas): N, 11.75.

N-Acetylbenzene-hydrazo-*o*-toluene, m. p. 78°.

Anal. Calcd. for $C_{15}H_{16}ON_2$: N, 11.66. Found (micro-Dumas): N, 11.47.

N-Acetyl-p-chlorohydrazobenzene, m. p. 123–124°.

Anal. Calcd. for $C_{14}H_{13}ON_2Cl$: N, 10.74. Found (micro-Dumas): N, 10.62.

N′-Acetyl-*p*-chlorohydrazobenzene, m. p. 111–112°.

Anal. Calcd. for $C_{14}H_{13}ON_2Cl$: N, 10.74. Found (micro-Dumas): N, 10.82

N′-Acetyl-*p*-bromohydrazobenzene, m. p. 83°, prisms from 90–120" ligroin.

Anal. Calcd. for $C_{14}H_{13}ON_2Br$: N, 9.18. Found (micro-Dumas): N, 8.97.

N-Acetyl-p-bromohydrazobenzene, rosets of prismatic crystals from alcohol, m. p. 117–118°.

Anal. Calcd. for $C_{14}H_{13}ON_2Br$: N, 9.18. Found (micro-Dumas): N, 9.42.

Isomeric Form of **N-Acetyl-*p*-bromohydrazobenzene.**—In the course of one experiment, N-acetyl-*p*-bromohydrazobenzene was recrystallized from alcohol containing about 10% of benzene. In addition to the N-acetyl derivative already described, a second product consisting of large cubical crystals was deposited on spontaneous evaporation of a part of the mother liquor. This substance melted at 88–89'. It was analyzed directly after isolation.

Anal. Calcd. for $C_{14}H_{13}ON_2Br$: N, 9.18. Found (micro-Dumas): N, 9.70.

After standing for two or three months in a closed vessel, the cubical crystals were found to have crumbled slowly to a white opaque powder. The latter melted at 117–118" and was identical with the stable N-isomer.

Identification of the Acetyl Derivatives.—A small amount (3–5 g.) of the acetyl derivative was heated with an equimolar amount of phenylhydrazine at 180" until the evolution of nitrogen and ammonia had ceased. This usually required about six hours. The mixture was then dissolved in 2–3 cc. of glacial acetic acid with slight warming and then treated with 5 cc. of water. The amide was precipitated as an oil which slowly solidified. The solid mass was then recrystallized from benzene or toluene. In those cases where isomeric compounds were obtained, one of the isomers only was identified by this procedure. The identity of the second isomer was established from the following considerations: (1) its non-identity with the first, (2) analysis, **(3)** transformation to the azo compound by hydrolysis of the acetyl group followed by oxidation with hydrogen peroxide. The following members of the above series were identified by phenylhydrazine reduction: N'-acetylbenzene-hydrazo-p-toluene, N-acetylbenzene-hydrazo-*o*-toluene, N′-acetyl-*p*-chlorohydrazobenzene and N′-acetyl-*p*-bromohydrazobenzene.

Effect of Anilides on the Self-oxidation–Reduction of **Phenylhydrazine.**—The reduction of N-acetylbenzene-hydrazo-o-toluene was conducted in one experiment to secure an approximate measure of the rate of evolution of nitrogen; 0.565 g. of the substance and 0.25 g. of phenylhydrazine were heated at 175–180° and the nitrogen evolved was collected over dilute hydrochloric acid in an inverted graduated cylinder The volumes (cc.) evolved during successive five-minute intervals were (uncorr.): 5.0, 9.5, 12.5, 10 0, 7.0, 6.0, 4.0. The rapid increase in rate during the first fifteen minutes suggested the following experiments on the effect of acetanilide and acet-*m*-toluidide in the self-oxidation–reduction of phenylhydrazine.

(a) **Acetanilide.**—1.35 g. of acetanilide and 1.08 g. of phenylhydrazine were heated at 185" and the evolved gases collected over water in a graduated cylinder. The presence of ammonia in the gaseous products was detected by its odor and action on litmus, and a layer of benzene appeared on the surface of the water in the graduated cylinder. After the reaction had ceased, 110 cc. of nitrogen (corrected for temperature, pressure, water vapor and benzene vapor) had been collected. This corresponds almost exactly to the volume of nitrogen theoretically obtainable by the self-oxidation–reduction of phenylhydrazine (112 cc.). The reaction mixture solidified on cooling. The crystals after washing with benzene melted at 114–115° and were shown to be acetanilide by comparison with an authentic sample of the latter.

(b) Acet-m-toluidide.4.822 gram of acet-m-toluidide and 0.608 g. of phenylhydrazine were heated at 150–160°, as in (a). The nitrogen evolved measured 63 cc. (corr.); the theoretical nitrogen volume is 63 cc. The reaction mixture was dissolved in 1 cc. of glacial acetic acid and the solution slowly diluted with 5 cc. of water. An oil separated which was washed with hot water and allowed to cool. It was then seeded with a small crystal of acet-m-toluidide and allowed to stand for twenty-four hours. The oil solidified completely; the crystals were pressed dry on filter papers and found to melt at 67–68". The crystalline product was acet-m-toluidide which underwent no change during the reaction.

Modified Procedure for Reduction with **Phenylhydrazine.**—The point at which the reduction of the acetylhydrazo compound with phenylhydrazine is complete was determined in the case of a mono-acetylbenzene-hydrazo-m-toluene(not described in this communication) in the following manner: 1.33 g. (1 mol) of acetylhydrazo compound and 1.8 g. (3 mols) of phenylhydrazine were heated at 160° until gases ceased to be evolved. Then 0.16 g. of phenylhydrazine was added, the mixture again heated and the evolved nitrogen collected and measured. It was found that 25 cc. (corr.) was evolved; 0.16 g. of phenylhydrazine should yield 16.6 cc. when undergoing complete self-oxidation–reduction; the reduction of the acetyl hydrazo compound was therefore incomplete. An additional 0.16 g. of phenylhydrazine was added, the heating continued at 160°, and the volume of nitrogen again measured. This time 17.1 cc. (corr.) was collected, indicating that the reduction was practically complete, inasmuch as the newly added phenylhydrazine underwent only self-oxidation–reduction.

Summary

1. Several new diaryl acyl hydrazines have been prepared.

2. A method for their identification has been described.

3. The self-oxidation–reduction of phenylhydrazine has been shown to be accelerated by acetanilide and acet-m-toluidide.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

PREPARATION OF SOME ORGANO–MERCURIC NITRATES, AND A METHOD OF ANALYSIS FOR MERCURY APPLICABLE TO DILUTE SOLUTIONS OF SUCH COMPOUNDS

BY I. B. JOHNS, W. D. PETERSON AND R. M. HIXON

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In continuing the studies on the "electron-sharing ability of organic radicals,"[1] a series of organo–mercuric derivatives has been prepared and carefully purified for the measurements of physical constants which will be reported later. It was found necessary to develop a method of analysis for the determination of the organo–mercuric compounds when present in dilute aqueous solutions. This method depends upon the liberation of mercury from its organic linkage by refluxing with aqueous bromine and later precipitating and weighing the mercury as the sulfide. The method has also been applied to the determination of mercury in the pure organo-mercuric derivative. In the presence of iodides, a double precipitation of the sulfide is necessary.

The type compounds $RHgNO_3$ were prepared by treating the corresponding halides in a suitable solvent with silver nitrate. The butyl- and benzylmercuric nitrates have not been previously reported; the melting points and statements regarding the stability of the methyl- and ethylmercuric nitrates are corrected.

Experimental

Methylmercuric Nitrate.—To a weighed quantity of silver nitrate a slight excess of methylmercuric iodide is added and shaken in ethyl alcohol until the filtrate gives no test for silver ions. The solution is diluted with water, warmed and filtered with suction and evaporated over a water-bath in a current of air. The product is recrystallized twice from water by concentrating the solution until a crystalline mush is obtained and then removing the mother liquor by pressing between filter papers. The crystals are dried *in vacuo*. The product is white, stable in light, strongly deliquescent, and causes painful blisters if applied to the skin. Samples have been kept for two years without becoming discolored.

The melting point, unlike that given in the literature,[2] is 59°, obtained in two independent preparations and constant through successive recrystallizations.

Anal. Calcd. for CH_3HgNO_3: Hg, 72.26. Found: Hg, 72.24, 72.72.

The conductivity in water checks the values reported by Maynard and Howard,[3] though they gave no melting point.

Ethylmercuric nitrate was prepared in the same way as the methyl compound, is less soluble and recrystallizes more easily, giving a better yield. The melting point, not reported by Strecker,[2] who first prepared it, is 87°.

Anal. Calcd. for $C_2H_5HgNO_3$: Hg, 68.79. Found: Hg, 68.85, 68.42.

The solubility in water at 25° is 6.96 g. per liter.

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[1] Hixon and Johns, THIS JOURNAL, 49,1786 (1927).

[2] Strecker, *Ann.*, 92, 79 (1854).

[3] Maynard and Howard, *J. Chem. Soc.*, 123,960 (1923).

Butylmercuric nitrate was prepared from the bromide and silver nitrate. It was found to be very unstable until carefully recrystallized from ether. It was never obtained entirely colorless, and always decomposed slightly on standing for several months; m. p. 39.5–40°.

Anal. Calcd. for $C_4H_9HgNO_3$: C, 15.02; H, 2.84; N, 4.38. Found: C, 14.80, H, 2.89; N, 4.44.

The solubility in water at 25° is 0.956 g. per liter.

Benzylmercuric nitrate is best prepared by mixing a solution of benzylmercuric chloride in ether with silver nitrate in alcohol. After shaking for an hour, the silver chloride is filtered off and the solvent evaporated at as low a temperature as possible *in vacuo.* In this way, 11.35 g. of benzylmercuric chloride and 5.89 g. of silver nitrate gave 4.95 g. of silver chloride (theoretical, 4.97 g.). The resulting benzylmercuric nitrate was a gray crystalline mass. Recrystallized from ether, it gave large, pure white, rhombic needles; m. p. 90–91° with decomp.

Anal. Calcd. for $C_6H_5CH_2HgNO_3$: Hg, 56.71. Found: Hg, 56.64, 57.05.

The solubility in water at 25° is 0.93 g. per liter. In spite of all care in preparation, the compound slowly decomposes and after several months appears dark, though still crystalline.

Method of Analysis for Mercury in Organo-mercuric Halides and Nitrates.—In analyzing a solid compound, sufficient sample to give 0.25 g. of mercuric sulfide is covered with 100 cc. of water and treated with 5 cc. of bromine. The flask is heated gently and finally boiled to remove the excess of bromine. The last traces of bromine are removed by a few drops of sodium bisulfite solution[4] and the mercury is determined by the usual method. In case the organic radical forms oily bromination products, as occurs with many aromatic mercury derivatives, these may be removed by filtering through a paper filter.

The success of this method of decomposing organic compounds of mercury is indicated by the data in Table I. The method has been found equally successful in analyzing very dilute solutions of these compounds.

The quantitative precipitation of mercury as the sulfide is difficult when iodides are present.[5] This difficulty can be eliminated by applying the double precipitation method used by Scott[6] in separating mercuric sulfide from lead sulfide. In this method the precipitated mercuric sulfide is dissolved in potassium acid sulfide solution and reprecipitated by adding *a* solution of ammonium nitrate, boiling gently to expel most of the liberated ammonia. This second precipitate is then filtered onto a Gooch crucible and treated in the usual way.

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[4] Contrary to statements in textbooks, sulfur dioxide has not been found to reduce mercury in solution. A slight excess of sodium bisulfite in these acid solutions causes no trouble.

[5] Dunning and Farinholt, THIS JOURNAL, 51, 807 (1929), report the necessity of removing iodine. Reinders, *Z. physik. Chem.*, **32,** 498 (1900), considers digestion of the precipitated mercuric sulfide with ammonium chloride solution as sufficient to remove this difficulty.

[6] Scott, "Standard Methods of Chemical Analysis," 4th ed., **1927,** p. 310.

TABLE I

ANALYTICAL DATA

Compound	Sample, g.	HgS found, g.	HgS calcd., g.
C_4H_9HgBr	0.2283	0.1580	0.1574
C_4H_9HgBr	.2551	.1763	.1758
CH_3HgNO_3	.3504	.2935	.2936
CH_3HgNO_3	.2736	.2307	.2292
$C_2H_5HgNO_3$	.1428	.1140	.1139
$C_2H_5HgNO_3$	.1573	.1248	.1255
$C_6H_5CH_2HgNO_3$	.1614	.1060	.1062
$C_6H_5CH_2HgNO_3$	.1693	.1120	.1114
o-$ClC_6H_4CH_2HgBr$[a]	.5000	.2859	.2865
	.5000	.2873	.2865
o-$ClC_6H_4CH_2HgAc$[a]	.3000	.1822	.1813
	.3000	.1817	.1813
(o-$ClC_6H_4CH_2)_2Hg$[a]	.5000	.2565	.2576
	.5000	.2581	.2576
o-$ClC_6H_4CH_2HgCl$[b]	.2000	.1282	.1287
	.2000	.1287	.1287
$C_6H_5(CH_2)_2HgBr$[c]	.3574	.2158	.2157
	.4412	.2676	.2662

[a] Analyzed by F. E. Ware. [b] By E. H. C. Fang. [c] By Florence Hooper.

In analyzing 0.025 molal mercuric iodide solutions that were 0.05 molal in potassium iodide, the first precipitate when weighed was found to be approximately 4% too heavy while, when reprecipitated, the weight both with mercuric iodide and with methylmercuric iodide was found to agree within 0.1% with the calculated values.

Summary

1. The purification of methyl- and ethylmercuric nitrates is described and the melting points of these compounds are corrected.
2. Butyl- and benzylmercuric nitrates are described.
3. A rapid method of analysis for mercury in the type compounds RHg-X is described which is satisfactory even in the presence of iodides.

AMES, IOWA

[Contribution from the Department of Chemistry of the University of Colorado]

THE ACTION OF SODIUM ON SOME ORGANIC HALIDES IN LIQUID AMMONIA[1]

By Paul M. Dean and Gerard Berchet

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In the course of an investigation of the action of sodium on benzyl chloride,[2] it was observed that in liquid ammonia a good yield of dibenzyl was obtained, together with toluene and other non-nitrogenous products. The work of previous investigators, particularly Lebeau,[3] Chablay,[4] Kraus,[5] Picon,[6] Dains[7] and others, has shown that, as a rule, in this solvent the organic halogen compounds yield mixtures of amines, nitriles and unsaturated hydrocarbons.

In order to determine to what extent coupling reactions in the sense of the Wurtz–Fittig synthesis might take place, the following organic halogen compounds were investigated: benzyl chloride, 1-phenyl-2-bromo-ethane, 1-phenyl-3-bromopropane, 1-phenyl-4-bromobutane, benzal chloride, benzo-trichloride, diphenyldichloromethane, diphenylchloromethane, *o*-xylylene bromide, β-bromophenylethyl ether, γ-bromophenylpropyl ether, 6-chloro-acetophenone, β-chloropropiophenone. Chlorobenzene and triphenylchloromethane, which should be considered in this group, have already been investigated by White[8] and Kraus and Kawamura,[9] respectively. The first compound yields benzene and primary, secondary and tertiary amines, while the second yields the sodium salt of triphenylmethane which, in turn, enters into various reactions.

Benzoyl chloride, which also might be considered here, reacts instantaneously with the liquid ammonia to give an almost quantitative yield of benzamide. This reaction furnishes a very convenient method for the preparation of the amide.

Apparatus and Procedure

About 250 cc. of anhydrous ammonia was placed in an unsilvered Dewar flask of 300-cc. capacity. The halide and sodium were added in small

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[1] Abstracted from a thesis presented by Gerard Berchet to the Graduate Faculty of the University of Colorado in partial fulfilment of the requirements for the Doctor of Philosophy degree

[2] A detailed report of the action of sodium on benzyl chloride in liquid ammonia, in ether, and in the absence of solvent will be published later.

[3] Lebeau, *Compt rend.*, 140, 1042, 1264 (1905).

[4] Chablay, Ann *chim.*, [9] 1, 469 (1914).

[5] Kraus and White, This Journal, 45, 7G8 (1923)

[6] Picon, Bull. *soc. chim* , 35, 979 (1924)

[7] Dains and Brewster, This Journal, 42, 1573 (1920).

[8] White, *ibid* , 45, 779 (1923).

[9] Kraus and Kawamura, *ibid* , 45, 2756 (1923).

portions alternately. In most of the experiments the blue color of the dissolved sodium was allowed to disappear before further addition of the metal. In those preparations in which the reaction seemed to be slow, the flask was equipped with a mechanical stirrer and mercury seal. It was not deemed necessary to protect the reaction mixture from atmospheric gases because the rapid evaporation of the ammonia prevented the entrance of air into the flask.

After the completion of the reaction, the contents of the flask were poured into a casserole and the solvent was allowed to evaporate. The residue was then treated with a mixture of ether and water, the ether layer separated, and the aqueous layer extracted several times with fresh portions of ether. The combined ether solutions were dried over calcium chloride, the ether was distilled and the residue investigated. Except in the cases of β-bromophenylethyl ether and y-bromophenylpropyl ether the aqueous layer was not investigated further.

Experimental

Benzyl Chloride.[10]—Three hundred grams of benzyl chloride was treated with the calculated amount of sodium—1 mole of sodium to 1 mole of chloride—in several runs and the residues were combined. Brightly colored red and purple intermediate products formed and disappeared during the course of the reaction. The combined residues were taken up with a mixture of ether and water, after which treatment a solid--4.5 g.—was left. After separating the ether layer, the aqueous solution was extracted several times with fresh portions of ether. The combined ether solutions were then dried over calcium chloride. The ether was distilled through a Vigreux column, after which 25 g. of toluene came over between 95 and 110° at 629 mm. The residue—181 g.—was then fractionated under reduced pressure. At first a few drops of unchanged benzyl chloride came over; then the temperature rose rapidly. At 150–155° under 17 mm. pressure, 94 g. of dibenzyl came over. The residue in the flask, a viscous oil, was treated with ether. A solid weighing 5.1 g. separated. This proved to be identical with the 4.5 g. of white solid separated in the first phase of the reaction. This substance was referred to as "Solid A." It proved to be a hydrocarbon which crystallized from chloroform–alcohol and melted at 183–184°. After distilling the ether, the viscous oil was again fractionated under reduced pressure. An additional 14 g. of dibenzyl was obtained, together with 37 g. of a liquid—"Liquid B"—which distilled at 200–240" under a pressure of 10 mm., and finally 13 g. of a very viscous oil which distilled between 240 and 270" under 10 mm. pressure. This was referred to as "Liquid C" The residue in the flask weighed 9 g. All of the products were nitrogen and halogen free. The yields were as follows: toluene, 25 g; dibenzyl, 108 g.; Solid A, 9.5 g., Liquid B, 37 g.; Liquid C, 13 g.; residue, 9 g.

1-Phenyl-2-bromo-ethane.—This compound was prepared from phenylethyl alcohol by the Norris[11] method. It reacted rapidly with sodium in liquid ammonia in the ratio of 1 mole of halide to 1.9 moles of sodium. The following products were obtained from the ether extracts of the reaction products of 66 g. of the halide: ethyl-

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[10] Since this paper was submitted, an article by Wooster and Mitchell has appeared in which an account of the action of sodium and potassium on benzyl bromide in liquid ammonia is given [THIS JOURNAL, 52, 693 (1930)).

[11] Norris, Watt and Thomas, *ibid.*, 38, 1071 (1916).

benzene, 14.5 g.; styrene, 0.5 g.; residue (nitrogen free), 7 g. The residue consisted of high-boiling hydrocarbons from which no 1,4-diphenylbutane could be obtained.

1-Phenyl-3-bromopropane.—Fifty g. of the halide required 6.6 g. of sodium—ratio 1:1.5. The residue weighing 28 g. yielded the following products: propylbenzene, 8.5 g.; phenylpropylamine, 5.9 g.; high-boiling hydrocarbons, 3 g.; residue containing nitrogen, 7 g.; diphenylhexane, none.

1-Phenyl-4-bromobutane.—This substance reacted with the sodium in the ratio 1:1.5. From 9.3 g of the halide the following products were obtained. butylbenzene, 2.5 g.; unsaturated hydrocarbons, 0.05 g.; phenylbutylamine, 1.04 g.; hydrocarbons and amines, 1.6 g.

Benzal Chloride.—The reaction in the case of benzal chloride was more violent than in that of benzyl chloride. The sodium was used in the ratio 2:1. During the course of the reaction a bright red coloration developed which did not disappear until the ether–water mixture was added at the end of the experiment. Sixty grams of the chloride was used. The following products were obtained from the residue: dibenzyl, 2.5 g.; benzylamine, 15.0 g.; higher-boiling amines and residue, 14.0 g.

Benzotrichloride.—In this reaction the trichloride required approximately 3 moles of sodium. A rather large amount of tarry matter, insoluble in ether, along with about 5% of dibenzyl, was obtained. The tarry matter contained nitrogen.

Diphenylchloromethane.—On account of the slight solubility of the chloride in the ammonia, the reaction was slow. The addition of anhydrous ether considerably hastened the reaction. Twenty-four grams of the halide required 4.3 g. of sodium—ratio 1:1.59. It was difficult to determine the end-point of the reaction on account of the dark brown color of the mixture. On treatment of the residue with the ether–water mixture, a white solid, identified as *sym.*-tetraphenylethane, separated. From the ether layer a second portion of this hydrocarbon together with diphenylmethane was obtained. The total yield of these two compounds was 13 and 5.5 g., respectively. No other products were obtained from the ether layer.

Diphenyldichloromethane.—As in the case of diphenylchloromethane the reaction was slow until dry ether was added to the reaction mixture. In this experiment 31.5 g. of the halide was treated with sodium in the molecular ratio of 1:2. Care was taken to keep the halide in excess until the end of the reaction. After treating the residue with the ether–water mixture, 16 g. of a solid remained which on purification proved to be tetraphenylethylene. An additional 3.8 g. of tetraphenylethylene was obtained from the ether extract. The 19.8 g. of tetraphenylethylene obtained from the 31.5 g. of the diphenyldichloromethane corresponds to a yield of 90% of the theoretical. This method of preparation compares favorably with that of Norris.[12] The conversion of the tetraphenylethylene into tetraphenylethane seems to be effectively prevented by the method of procedure in which the sodium is added in small portions to an excess of halide until the ratio 1:2 is reached.

o-Xylylene Bromide.—On account of the slowness of the reaction even in the presence of anhydrous ether, the Dewar flask was fitted with a mechanical stirrer and mercury seal. Two moles of sodium were required for 1 mole of the bromide. The yield obtained from 25 g. of o-xylylene bromide consisted of 3.1 g. of o-xylene and 5.8 g. of a residue containing nitrogen.

p-Bromophenylethyl Ether.—In this case the reaction took place vigorously and smoothly, without the formation of intermediate colored compounds. The ratio of halide to sodium was 1:2. From 21 g. of β-bromophenylethyl ether the following compounds were obtained: 1,4-diphenoxybutane, 2.9 g.; phenol, 7.0 g.

γ-Bromophenylpropyl Ether.—This compound reacted rapidly and smoothly with

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[12] Norris, Ber., 47, 473 (1914).

sodium in the ratio 1:1.82. No intermediate colored compounds were observed. From 52 g. of the bromide a residue weighing 25.5 g. was obtained. This consisted of a mixture of colorless crystals and a mobile liquid, both of which were nitrogen free. From this mixture the following products were obtained: phenoxypropane,[13] 14.8 g.; phenol, 6.0 g.; 1,6-diphenoxyhexane, 4.4 g.

a-Chloro-acetophenone.—The halide reacted with sodium in the ratio 1:2.2. From 30 g. of the chloro-acetophenone, 13.5 g. of a reddish oil was obtained. This was nitrogen and halogen free. Four grams of acetophenone was separated from this oil; 0.4 g. of a colorless solid, melting at 73–74°, was also obtained, but was not identified. The residue yields, for the most part, tarry matter when it is distilled.

β-Chloropropiophenone.—In this case the reaction with sodium is rapid although the β-chloropropiophenone is not very soluble in the ammonia. The reaction takes place in the ratio of halide to sodium of 1:1.53. From 16 g. of the chloride a residue weighing 11 g. was obtained. This was a viscous oil, slightly fluorescent in solution, and nitrogen and halogen free. It did not boil at 380° under 20 mm. pressure. On cooling it solidified to a hard resin.

Conclusions

The limited number of halogen compounds studied does not permit one to draw definite conclusions regarding the relation of the structure of the molecule to the products formed. In the cases of the monohalogen compounds the following reactions indicate a possible mechanism

$$\begin{aligned}
MCH_2X + 2Na &\longrightarrow (MCH_2Na) + NaX && \text{(I)}\\
(MCH_2Na) + MCH_2X &\longrightarrow MCH_2CH_2M + NaX &&\\
MCH_2Na + NH_3 &\longrightarrow MCH_3 + NaNH_2 && \text{(II)}\\
MCH_2X + NaNH_2 &\longrightarrow MCH_2NH_2 + NaX && \text{(III)}\\
2C_6H_5O(CH_2)_2Br + 2Na &\longrightarrow 2NaBr + C_6H_5O(CH_2)_4O(C_6H_5) && \text{(IV)}\\
C_6H_5O(CH_2)_2Br + 2Na &\longrightarrow NaBr + C_6H_5ONa + C_2H_4{}^{14} &&
\end{aligned}$$

The reactions must be much more complicated in the cases of the polyhalogen compounds, as, for example, when nitriles are formed.[15]

Summary

1. The action of sodium in liquid ammonia on thirteen organic halogen compounds has been studied.
2. In eight cases a reaction in the sense of the Wurtz–Fittig synthesis took place to some extent.
3. Convenient methods for the preparation of benzamide, tetraphenylethylene and tetraphenylethane have been suggested.

BOULDER, COLORADO

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[13] Dionneau, *Ann. chim.*, 3, 201 (1915).

[14] Hamonet, *Compt.* rend., 136, 96 (1903).

[15] Dains and Brewster, THIS JOURNAL, 42, 1573 (1920).

[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

THE BROMINATION OF ACETONE IN ORGANIC SOLVENTS[1]

BY IRVING COHEN

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Introduction

The halogenation of ketones has offered a fertile field to investigators. Lapworth,[2] Dawson[3] and Rice[4] have made the most specialized contributions to this topic. Since these workers confined their studies mainly to reactions in aqueous solutions catalyzed by acids, an investigation of the natural autocatalytic reaction between acetone and bromine was carried out.

Purification of Materials

Acetone was purified by the sodium iodide addition-compound process of Shipsey and Werner.[5] A few minor changes were necessary to insure an anhydrous product. The acetone resulting from the iodide process was allowed to stand over phosphoric oxide for twenty-four hours. A deep red coloration appeared. On fractionation, discarding the first few cc., a material boiling at 56 38 ± 0 01° was obtained; density at 0°, 0.8035; at 25°, 0.7886.

Bromine was extracted three times with 10% sodium hydroxide solution and then distilled in an all-glass apparatus, once alone, and twice over phosphoric oxide.

Carbon tetrachloride was fractionated nine or ten times over phosphoric oxide until three liters distilled at 76.70–76 83°.

Carbon bisulfide was allowed to stand over bright, clean mercury for two weeks. It was then fractionated over phosphoric oxide; b. p 46.10 ± 0.01°.

Chloroform was purified immediately before use Technical chloroform was washed with water to free it from alcohol. It was then dried over calcium chloride and fractionated over phosphoric oxide; b. p. 61.30 ± 0.02° at 769 mm.

Apparatus

In the first part of this investigation the reaction was followed by titration of the bromine. Two hundred and fifty-cc. volumetric flasks were immersed in ice shavings. One hundred cc. of solvent at the bath temperature was pipetted into the flask. A small vial containing a weighed amount of bromine was dropped into the solvent, the ground glass stopper being removed as it fell. The flask was then well shaken and the reaction started by adding a known amount of acetone, usually 10 cc. Samples were withdrawn after suitable intervals, run into potassium iodide solution and titrated immediately with 0.05 N sodium thiosulfate.

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[1] This article is based on a thesis submitted by Irving Cohen to the Faculty of the Rensselaer Polytechnic Institute in partial fulfilment of the requirements for the degree of Master of Science.

[2] Lapworth, J. *Chem. Soc.*, **85**, 30 (1904); **93**, 2163 (1906); **95**, 2187 (1908).

[3] Dawson, *ibid.*, 96, 1860 (1909); **98**, 2048 (1910); **101**, 1503 (1912); **105**, 1093 (1914).

[4] Rice, THIS JOURNAL, 47, 379 (1925).

[5] Shipsey and Werner, J. *Chem. Soc.*, **103**, 1255 (1913).

In the second part of the investigation the reaction was determined by following the change in conductivity of the reaction solution. Assuming that hydrobromic acid is the only substance formed which can affect the conductivity, the conductance of these solutions affords a measure of the concentration of the acid at any time. Since the specific conductance of these solutions approaches the order of 10^{-9} mhos per centimeter, special equipment was necessary.

Conductance Cell.—Dipping electrodes of polished platinum, 6.5 by **3** cm., mounted approximately 4 mm. apart, and fastened together firmly by glass rivets, were used. This combination was sealed on a glass tube having leads for connections through the tube. Since these electrodes were not platinized and exerted a large condenser action in water, it was difficult to obtain an accurate cell constant using the potassium chloride solutions of Washburn. The mean of a number of determinations gave 0.0218 ± 0.009. Because of the large uncertainty in the cell constant, all readings are given as the observed cell conductance, these values being easily reproduced to within 0.5%. The electrodes were not platinized for two reasons: (1) platinization might catalyze the reaction, (2) gaseous hydrobromic acid might be adsorbed due to the increased surface.

Resistance Box.—It was necessary to use resistances as non-inductive as possible. Three boxes, type 102J, serial No. 868 made by the General Radio Company of Cambridge, Massachusetts, were available, giving a possible variable resistance from 0 to 33,000 ohms.

Variable Air Condenser.—In order to balance the bridge satisfactorily, the capacitance of the conductance cell must be tuned out by a variable condenser. The instrument used had a capacity of 0 to 1500 m.m.f. and was made by the General Radio Company, being type 246L and serial No. 335.

Vacuum Tube Oscillator.—This was the Western Electric 4-B oscillator delivering frequencies of 100 to 5000 cycles per second. The output was capable of fine adjustment, so that during an experiment in which the conductance varied between wide limits, it could be varied to suit the need.

Slide Wire Bridge.—A Leeds and Northrup Slide Wire Bridge having a high resistance per unit length of wire was used. This sacrifices some precision but has the advantage of having the balance occur at exactly one point on the bridge wire. This condition is imperative when the conductance is changing rapidly with time.

Telephones.—These phones were made by S. G. Brown, Ltd., of London. They are equipped with a mechanical tuning device and were especially designed for conductivity work.

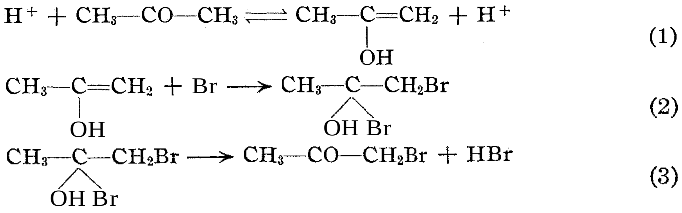
The procedure for determining a typical reaction velocity by the conductance method was as follows. Twenty cc. of acetone was pipetted into a glass cylinder. A vial containing a weighed amount of water was introduced and the acetone whirled in the cylinder. One hundred and twenty-five cc. of carbon tetrachloride was added and the liquids mixed thoroughly. A cork carrying the mounted electrodes was inserted into the cylinder and the latter immersed in a thermostat kept at $25.00 \pm 0.01°$. After a half hour had elapsed, a second vial containing a weighed amount of bromine was dropped into the solution by means of a glass tube leading through the cork. The time of adding the bromine was taken as the zero time of the reaction. The solution was always shaken for thirty seconds to allow the bromine to distribute itself equally throughout the solution. At suitable intervals, time and bridge wire readings were taken.

To obtain a reading, the following steps were required. The switch to the oscillator was closed. The bridge was then balanced to a minimum of sound, next the air condenser, and so alternately until a final balance on the bridge was obtained. The time was taken to the nearest five seconds and the switch to the oscillator opened. The entire procedure took at most ten seconds.

In assembling the above apparatus, the principles of design advocated by Washburn,[6] Morgan and Lammert[7] and Taylor and Acree[8] were used.

Theory and Results of Experiments

Lapworth[9] has explained the reaction of acetone with the halogens by means of the equations:



$$H^+ + CH_3{-}CO{-}CH_3 \rightleftharpoons CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}}{=}CH_2 + H^+ \qquad (1)$$

$$CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}}{=}CH_2 + Br \longrightarrow CH_3{-}\underset{OH\ Br}{\underset{/\ \backslash}{C}}{-}CH_2Br \qquad (2)$$

$$CH_3{-}\underset{OH\ Br}{\underset{/\ \backslash}{C}}{-}CH_2Br \longrightarrow CH_3{-}CO{-}CH_2Br + HBr \qquad (3)$$

Reactions 2 and 3 were assumed to be practically instantaneous, while the rate of attaining the keto–enol tautomeric equilibrium expressed by Reaction 1 was assumed to be comparatively slow. This mechanism explained why the velocity of this reaction was independent of the concentration of the bromine. It was also observed that the reaction was enormously catalyzed by hydrogen ions.

In order to ascertain the natural rate of reaction between acetone and bromine without using any solvent, 110 cc. of acetone and 0.840 g. of bromine were allowed to react. Figure 1 represents the concentration of bromine in 10 cc. of the mixture as a function of the time. The solution remains deep red until near the end of the reaction, when the liquid becomes lighter in color and then decolorizes practically instantaneously. From Fig. 1 it may be calculated that approximately 50% of the original bromine is converted into monobromo-acetone and hydrobromic acid during the last few seconds of

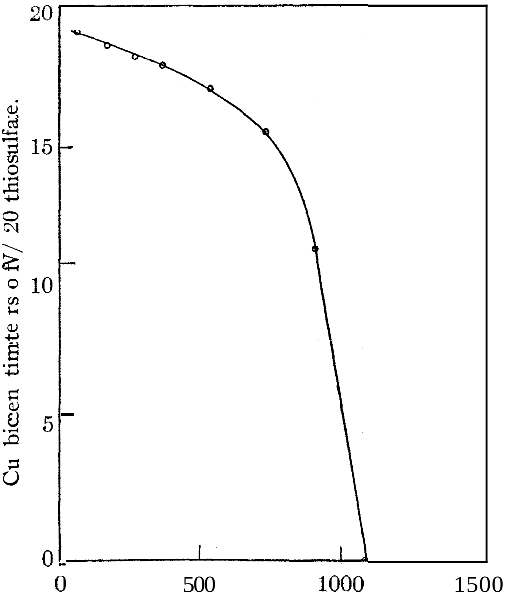


Fig. 1.—Temp., 0°; 110 cc. of acetone; 0.840 g. of bromine.

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[6] Washburn, THIS JOURNAL, **38,** 2431 (1916); **39, 238** (1917).

[7] Morgan and Lammert, *ibid.*, 45, 1692 (1923).

[8] Taylor and Acree, *ibid.*, **38,** 2396, 2403, 2415 (1916).

[9] Lapworth, J. Chem. *Soc.*, **85,** 30 (1904).

the reaction, thus indicating the high speed of the reaction at that time. Since hydrogen bromide is continually formed during the reaction, we should expect autocatalytic effects, *viz.*, the amount of bromine decomposed per unit time should be greater as the concentration of hydrogen bromide increases in the solution. Figure 1 shows that such is the case (see Table I).

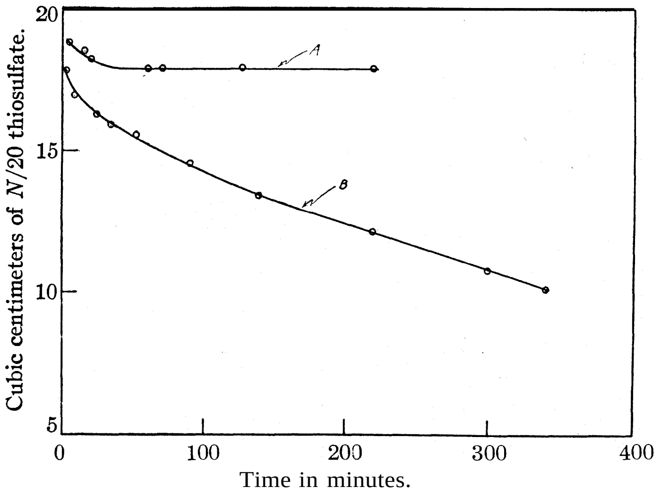

Fig. 2.—Temp., 0°; 110 cc. of acetone; 0.840 g. of bromine. Curve A, 0.50 g. of pyridine; Curve B, 0.70 g. of quinoline.

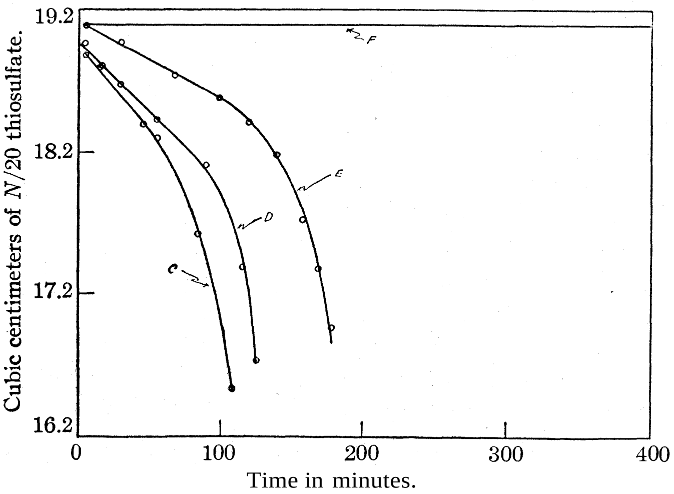

Fig. 3.—100 cc. of solvent; 10 cc. of acetone; 0.810 g. of bromine; temp., 0°. Solvents: Curve C, CS_2; D, $CHCl_3$; E, CCl_4; F, H_2O.

Effect on the Reaction of the Possible Removal of **HBr.**—In order to study the reaction without the catalytic influence of hydrogen bromide, substances were added which were supposed not to be affected by bromine and pet combine with hydrogen bromide as fast as it was formed. Curve A, Fig, 2, represents the result of this experiment. There seems to be no reaction after an initial disturbance. While these experiments were in progress, an article by Watson[10] appeared, in which it was stated that quinoline retarded the rate of halogenation of ketones but did not actually stop the reaction. Since pyridine and quinoline are closely related compounds this difference in behavior seemed odd. Curve B, Fig. 2, gives the results of a run using quinoline in place of pyridine. The difference in behavior can be explained by assuming different degrees of stability of the bromo addition compounds of pyridine and quinoline.

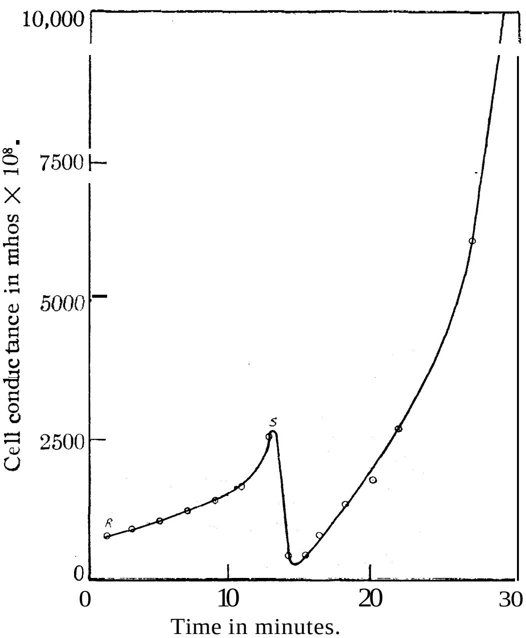

Fig. 4.

Effect of Various Solvents.—The reaction rate is affected by the solvent used, an extremely slow rate being observed for water, while maximum speed occurred with carbon disulfide as a solvent. Although the two other organic solvents (see Fig. 3) are chemically similar to carbon disulfide, they have a substantial influence on the reaction rate. We see also that the presence of a solvent does not change the general characteristics of the reaction (compare Figs. 1 and 3).

Effect of Varying Concentrations of Acetone and **Bromine** in Carbon **Tetrachloride.**—By suitably varying the concentrations of acetone and bromine, using carbon tetrachloride as solvent, it was found that the reaction rate was independent of the concentration of the bromine, while proportional to the concentration of the acetone.

The foregoing reactions were followed by titration. In the course of these experiments, some erratic results were obtained. The trouble was traced to water condensing on cold pipets and thus being introduced into the organic solvent. These small amounts of water were sufficient to practically stop the reaction. The effect of the addition of water to carbon tetrachloride on the rate of reaction of acetone and bromine was,

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[10] Watson, J. *Chem. Soc.*, 3065 (1927).

accordingly, investigated by a more accurate method, *viz.*, electrical conductance.

The conductance experiments were run at 25° since the conductances at 0° were of too low an order. Figure 4 represents a typical run on one of the carbon tetrachloride solutions. A few general observations apply to all of the solutions studied. (1) As soon as the solution decolorizes, it becomes turbid and fumes appear in the air space between the cork and the surface of the liquid in the cylinder. (2) Just after the point of decolorization, the resistance of the solution rises rapidly, usually exceeding the value of the initial resistance. Finally, the resistance decreases again to lower values. (3) The dielectric constant of the solution decreases considerably during the progress of the reaction.

At the point of decolorization a large quantity of bromine is converted into hydrogen bromide. On this basis, we would expect a very rapid rise in conductance but we find the reverse to be true. However, the solubility of gaseous hydrogen bromide in carbon tetrachloride is very small. When this large amount of gas is released throughout the solution it must of necessity be in the form of minute bubbles of gas surrounded by liquid. This cuts down the conducting area between electrodes and therefore raises the resistance. On shaking, the bubbles unite and leave the solution, thus making the area larger and decreasing the resistance. Figure 4 was obtained under just such experimental conditions. From R to S is that part of the curve in which we are interested. The readings from S to T are unessential for measurement of velocity constant and have therefore been omitted from all further data.

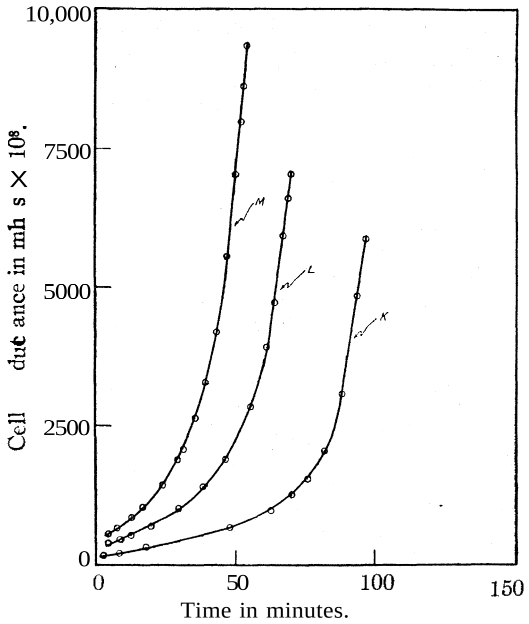

Fig. 5.—125 cc of carbon tetrachloride; 20 cc. of acetone; 0.743 g. of bromine; varying amounts of water; temp., 25°. Curve K, 0.229 g. of water; L, 0.180 g. of water; M, 0.160 g of water.

TABLE I

110 CC. OF ACETONE, 0.840 G. OF BROMINE. TEMP., 0°C.

Time, seconds.....	0	60	164	264	366	538	738	910	1086
0.05 N $Na_2S_2O_3$, cc.	...	19.05	18.56	18.20	17.83	17.05	15.50	11.25	0

Since the dimensions of the electrodes are fixed, any change in the adjustment of the condenser used for balancing must perforce come from a change in the dielectric constant of the solution whose conductance is being measured. All of the solutions exhibited a decrease in dielectric constant with time. This may be due to the gradual chemical combination of the water added initially, with some other compound.

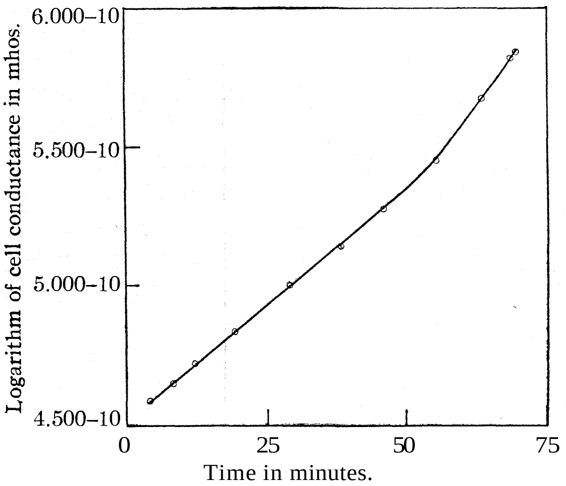

Fig. 6.—125 cc. of carbon tetrachloride; 20 cc. of acetone; 0.743 g. of bromine; 0.180 g. of water; temp., 25°.

On adding increasing amounts of water to a solution of 125 *cc.* of carbon tetrachloride and 20 cc. of acetone, the liquid becomes turbid at a certain point, due to the slight solubility of water in this mixture. The quantity

TABLE II

WITH CURVE M OF FIG. 5

125 cc. of carbon tetrachloride; 20 cc. of acetone; 0.743 g. of bromine; 0.160 g. of water; temp., 25°

Time, minutes	Cell conductance, mhos	Time, minutes	Cell conductance, mhos	Time, minutes	Cell conductance, mhos
3 00	0.00000501	21.17	0 00001305	41.00	0.00003699
4 25	556	23.00	1425	43.17	4185
5.25	577	25.00	1569	45.00	4781
7.00	652	27.00	1727	47.00	5554
8.33	692	29.00	1897	49.00	6681
9.00	716	31.00	2079	50.00	7036
10.00	758	33.17	2333	51.00	7455
12.17	850	35.33	2623	52.00	7990
14.00	937	37.00	2888	53.00	8624
16.00	1027	39.17	3271	54.17	9340
18.17	1127				

TABLE III

EXPERIMENTAL RESULTS FIG. 7

Velocity constant...	0.0136	0.0200	0.0264	0.0400	0 0434	0.0498
Mg. of water.......	229	180	160	98	90	61

of water necessary to cause the first appearance of turbidity was 100 mg. The turbidity seems to have no effect on the reaction, the water having an effect commensurate with what it would have in a clear, homogeneous solution. Figure 5 illustrates this fact. Curves K, L, and M, represent solutions containing 229, 180 and 160 milligrams of water, respectively (see Table II). Experiments run on clear solutions containing 98, 90 and 61 mg. of water give the same form of curve, with the rates of reaction increasing with decreasing amounts of water. It was impossible to obtain the reaction velocity of the anhydrous substances, the entire reaction being complete within thirty seconds.

Velocity constants were calculated by the method outlined below. Figure 7 represents the plot used for a typical calculation. The actual reaction deviates from the assumed law toward the end of the reaction.

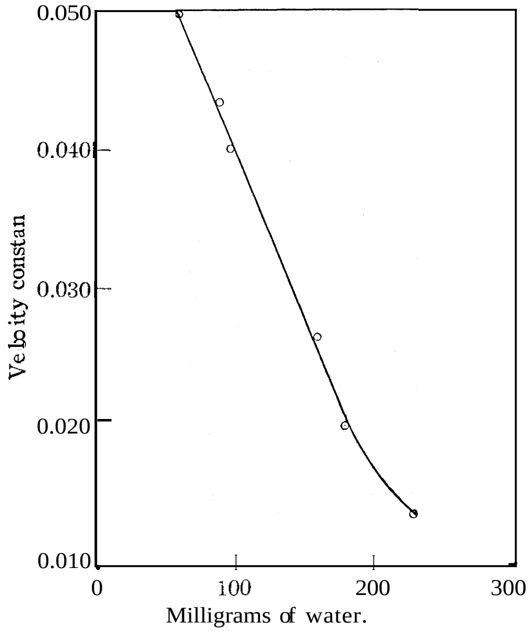

Fig. 7.

The numerical results of this investigation are given in Fig. 7. A very striking relationship is apparent. Water has an enormous retarding effect on this reaction and is no doubt intimately concerned in its mechanism.

Evaluation of Results

The sum total of all reactions occurring may be expressed as follows

$$CH_3COCH_3 + Br_2 \longrightarrow CH_3COCH_2Br + HBr$$

Let C_{HBr} = Concentration in moles per liter of hydrogen bromide at the time, t

C_A = Concentration in moles per liter of acetone. This may be considered constant for it is made large to insure the formation of monobromoacetone only

G = Conductance of the solution at the time, t

k = Velocity constant

K = Constant of proportionality between cell conductance and concentration of hydrogen bromide

G_0 = Constant of integration.

From our experiments we assume $d[C_{HBr}]/dt = kC_{HBr}\cdot C_A$. It is also necessary to assume $G = KC_{HBr}$. From these, $d[C_{HBr}]/dt = dG/Kdt = (kG/K)C_A$ or $dG/dt = kGC_A$. Integrating this equation and determining the value of the constant of integration by assuming a conductance due to a concentration of hydrogen bromide at the start of the reaction, we get $\ln G = kC_At + \ln G_0$, or passing to decimal logarithms and placing C_A = 1.874 moles per liter

$$\log G = \frac{1.874}{2.303}\,kt + \log G_0 = 0.8138\,kt + \log G_0$$

We can determine the numerical value of the velocity constant by plotting $\log G$ versus t, measuring the slope of the straight line obtained and dividing this value by 0.8138.

The author wishes to acknowledge his indebtedness to Dr. H. S. Van Klooster, Professor of Physical Chemistry at the Rensselaer Polytechnic Institute, under whose direction the investigation was carried out.

Summary

The kinetics of the bromination of acetone in organic solvents has been investigated.

Water has a powerful retarding influence on this reaction.

The extraordinary catalytic power of dry hydrogen bromide on the bromination of acetone is demonstrated.

The reaction is approximately first order with respect to hydrogen bromide.

A considerable change in the dielectric constant of the solutions used has been observed during the progress of this reaction.

TROY, NEW YORK

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE]

SULFONATION OF 2-NAPHTHOL IN PRESENCE OF BORIC ACID. 2-NAPHTHOL-1,6-DISULFONIC ACID

BY KARL H. ENGEL

RECEIVED JANUARY 25, 1930 PUBLISHED JULY 3, 1930

The use of boric acid as a catalyst in the sulfonation of 2-naphthol (one part of boric acid for two hundred parts of naphthol), for the purpose of improving yields and quality of the reaction products, has been patented by M. L. Crossley and G. S. Simpson.[1]

Two years before issue of the patent, the writer experimented in a similar direction, and observed that appreciable amounts of boric acid caused a striking change in the expected reaction course. A difference became outwardly noticeable—sulfonation masses, instead of remaining fluid, solidi-

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[1] Crossley and Simpson, U. S. Patent 1,570,046 (1926).

fied rapidly. With limited amounts of sulfuric acid the reaction led to the formation of 2-naphthol-1-sulfonic acid as a permanent, instead of a transitory, stage which in practice is rather difficult to arrest. Greater amounts of acid yielded mainly 2-naphthol-1,6-disulfonic acid, besides smaller amounts of the 8-sulfonic (Croceine) acid and only a few per cent. of the 6-sulfonic (Schaeffer) acid.

Fixed yield ratios of these three products, for definite reaction temperatures, were observed when one molecular weight of boric acid was used for three of naphthol. With gradually decreased amounts of boric acid, yield ratios changed continually; greater amounts had no further effect. Conceivably, then, formation of a trinaphthyl-boric ester preceded sulfonation. It may have been the sulfonated ester which caused solidification of sulfonation masses, but it decomposed immediately with water or ice.

The formation of 2-naphthol-1,6-disulfonic acid, though unlooked for, was in accord with the normal substitution tendencies of 2-naphthol, which may yield, as is well known, the 1-, the 6- and the 8-monosulfonic, the 3,6- and the 6,8-disulfonic and the 3,6,8-trisulfonic acids, no other but the 1-, 3-, 6- and &hydrogen atoms being replaceable upon direct sulfonation: of the naphthol.

The 1,6-disulfonic acid, undoubtedly, has been known for many years, but has received no more than cursory mention.[2] Presumably the product here referred to was prepared from the well-known naphthylamine-1,6-disulfonic acid.[3] More recently, J. Pollak and E. Blumenstock-Halward[4] prepared the 2-naphthol-1,B-disulfonyl chloride through the action of chlorosulfonic acid on naphthol or naphthol-6-sulfonic acid. Saponification of the chloride in alcoholic solution gave a tribarium and a tripotassium salt of the 1,6-disulfonic acid.

The 1,6-disulfonic acid resembled, in its chemical behavior, the naphthol-1-sulfonic acid. It could not be isolated as a free acid, but either sodium or potassium chloride precipitated it from solution in the form of its metal salts.

The sulfonic acid group in the 1-position prevented a smooth coupling with diazonium compounds, though more reactive ones, like *p*-diazobenzene, were capable of displacing the obstructing sulfonic acid group. The hydrolytic action of dilute acids likewise eliminated the same sulfonic acid group readily, at about 85°.

The ease with which the 1,6-disulfonic acid formed and its stability during sulfonation in presence of boric acid suggested that this product might also occur in sulfonations without the use of boric acid. It was indeed found to be a by-product in straight sulfonations at temperatures up to 75°,

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[2] H. Th. Bucherer, *J. prakt. Chem.*, [2] 177, 69–73 (1904); German Patent 117,471, and British Patent 1387 (1900).

[3] Forsling, *Ber.*, 21, 3495 (1888).

[4] J. Pollak and E. Blumenstock-Halward, *Monatsh.*, 49, 203 (1928).

and could be obtained as the main reaction product at temperatures under 18°. This observation made it possible, for the first time, to account for practically all of the conversion products of naphthol in sulfonation methods, which have long been used in the commercial production of the S- and 6-sulfonic and of the 6,8- and 3,6-disulfonic acids. (Higher sulfonation temperatures lead to other, poorly explained losses through destructive oxidation and perhaps through the formation of dehydration products of naphthol.)

A number of sulfonations were made, with or without addition of boric acid, to determine the specific influence of the latter, and to find the most suitable conditions for the preparation of the commercially important 2-naphthol-1-sulfonic and of the 1,6-disulfonic acid. The product yields of a few representative experiments have been tabulated below.

TABLE I

SULFONATION IN PRESENCE OF BORIC ACID

No. I	Naphthol/acid ratio, by wt	Temp., °C.	Time	Product yields, percentage of sulfonated naphthol 1-	6-	8-	1,6-di-
a[a]	1 to 2, 100% H_2SO_4	20–28	4 Min.	90	9	Trace	..
b	1 to 2, 94.2% H_2SO_4	30	24 Hr.	74	3	10	13
c	1 to 1.73, 94.2%	30	24 Hr.	83	3	5	9
d	1 to 10, 94.2%	0	30 Hr.	Trace	2	17	81
e	1 to 5, 94.2%	25	30 Hr.	Trace	3	21	76
f	1 to 3, 94.2%	45	30 Hr.	..	4	24	72
g	1 to 2, 94.2%	85	1 Hr.	..	20	27	53

[a] Incomplete reaction.

TABLE II

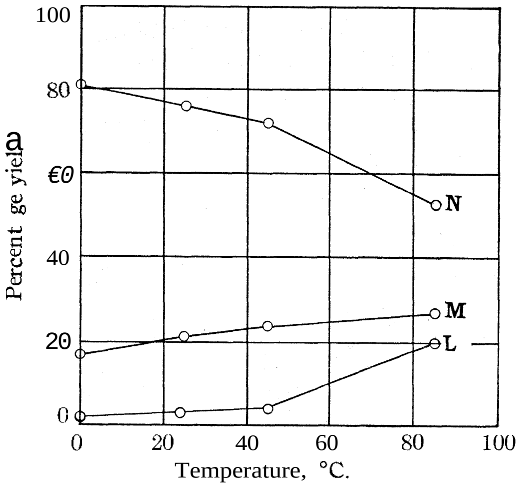
STRAIGHT SULFONATION

No II	Naphthol/acid ratio, by wt.	Temp , °C.	Time	Product yields, percentage of sulfonated naphthol 1-	6-	8-	1,6-di-
a[a]	1 to 2, 100% H_2SO_4	20–30	4 Min.	62	12	17	9
b	1 to 10, 94.2% H_2SO_4	2	24 Hr.	..	3	23	74
c	1 to 8, 94.2%	13	24 Hr.	..	7	31	61
d	1 to 5, 94.2%	18	24 Hr.	..	11	38	51
e	1 to 2, 94.2%	25	24 Hr.	..	23	54	23
f	1 to 2, 94.2%	28	24 Hr.	..	28	55	17
g	1 to 2, 94.2%	32	24 Hr.	..	33	54	12
h	1 to 2, 94.2%	45	24 Hr.	..	38	49	11
i	1 to 1.5, 94.2%	56	24 Hr.	..	47	46	7
k[b]	1 to 1 3, 94.2%	75	24 Hr.	..	60	28	1
l[b]	1 to 1.1, 94.2%	85	24 Hr.	..	74	11	..

[a] Incomplete reaction. [b] Unaccounted loss.

Discussion of Results

2-Naphthol-1-sulfonic Acid.—Sulfonation of brief duration, in presence of boric acid (Ia), led to the formation of only two products, the 1- and the 6-sulfonic acids, the former in a very attractive yield ratio. An appreciable quantity of naphthol, however, remained unsulfonated (though completely dissolved). If the time was extended, disulfonation took place as long as a sufficient concentration of sulfuric acid was available. For a most advantageous procedure the sulfuric acid concentration had to be so chosen as to allow complete sulfonation and, at the same time a minimum of disulfonation (Ic). To avoid all disulfonation did not appear feasible or even desirable, since the disulfonic acid could be more easily removed from the main product than the alternative by-product, the 6-sulfonic acid of Experiment Ia. Seventy-four per cent. of the naphthol could be recovered in the form of a 1-sulfonic acid, which was free from all but traces of isomers, by precipitating it from solution with sodium chloride and by washing the isolated sodium sulfonate with a saturated solution of the chloride.



N, 1,6-Disulfonic acid; M, 8-sulfonic acid; L, 6-sulfonic acid.

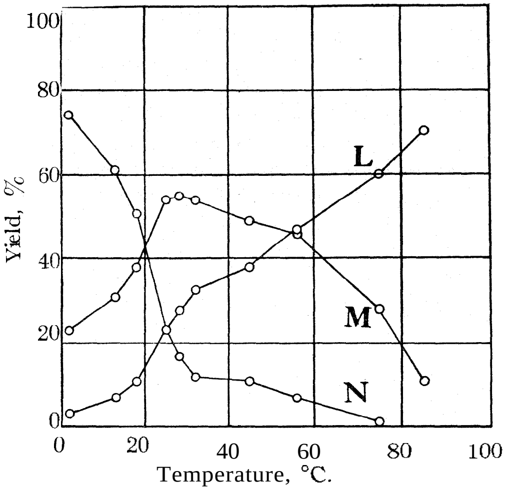
Fig. 1.—Sulfonation in presence of boric acid.

2-Naphthol-**1,6-disulfonic** Acid.— Sulfonations with concentrations of sulfuric acid sufficiently large to change all of the 1-sulfonic acid led to mixtures of the 1,6-disulfonic, the 6- and the 8-sulfonic acids. The latter two, in part at least, were rearrangement products of the former. The three products formed equilibrium mixtures, in which their yield ratios depended on the reaction temperatures. This relationship may be most conveniently illustrated by a graphic representation of data given in the preceding tables (Figs. 1 and 2). A further transformation of the three products into the 3,6- and 6,8-disulfonic acids proceeded very slowly below 35°, but more and more rapidly with rising temperatures. Where this change was not desired, the effect of higher temperatures could be counteracted, as is done in practice, by decreasing the reaction time or the acid concentration, or both.

Sulfonations in the presence of boric acid showed a very gradual change in yield ratios over the entire practical temperature range; the 1,6-disulfonic acid always predominated.

Striking peculiarities in the relationships between the three reaction products were observed in straight sulfonations (Fig. *2*). Between 0 and 18° yields of the dilsulfonic acid were surprising large. They decreased abruptly, however, within a narrow temperature range, the graph suggesting the existence of a critical temperature, at about 22°, above which the disulfonic acid molecule was no longer stable, but changed, rather impartially, into either the 6- or the 8-sulfonic acid. A conversion into the former, through hydrolysis of the 1-sulfonic group, might well be expected; a rearrangement into the 8-sulfonic acid should require a rather complicated mechanism.

The 2-naphthol-1,6-disulfonic acid could be prepared in practical yields either by a straight sulfonation or with the addition of boric acid, the latter method being the more convenient for its greater economy in materials and for the ease with which it may be controlled. Sulfonation at 45°, (If), appeared to be most suitable. The quantity of sulfuric acid used in this experiment might be further reduced by substituting a more concentrated (100%) acid.



L, 6-Sulfonic acid; M, 8 sulfonic acid; N, 1, 6-disulfonic acid.

Fig. 2.—Straight sulfonation.

Straight sulfonation experiments indicated that a reaction temperature of 25 to 30°, instead of the customary 45°, was most favorable for the commercial production of 2-naphthol-8-sulfonic acid, a maximum yield of the more expensive of the two isomers being obtained within this range. The by-product 1,6-disulfonic acid could be conveniently hydrolyzed into G-sulfonic acid by heating the diluted sulfonation mixture to 85°.

The 3,6- and 6,8-disulfonic ("R" and "G") acids require sulfonation temperatures at which the 1,6-isomer occurs in negligible amounts or not at all. Of interest might be a comparison of sulfonations, with or without addition of boric acid, at 135°. Sulfonation with three parts of concd. sulfuric acid to one of naphthol, at twenty-four hours' duration and in the presence of boric acid, yielded 28% of the 1,6-, 31% of the 6,8- and 39% of the 3,6-disulfonic acids. A straight sulfonation, under parallel conditions, gave 33% of the 6,8- and 43% of the 3,6- isomers, but no trace of the third isomer. The loss through destructive oxidation and other causes was considerable in this case, but negligible in the sulfonation with boric acid.

Experimental Part

Materials.—Resublimed 2-naphthol, which contained less than 0.1% of the isomeric naphthol, and pure concentrated sulfuric acid (94.2%) were used in sulfonations.

Acid of 100% strength was prepared by mixing calculated amounts of fuming and of concentrated acids. Pure boric acid was dehydrated at 110°; the resulting metaboric acid was readily soluble in sulfuric acid at 100 to 120° and was preferred to avoid unnecessary dilution of the sulfonating agent. The glassy boron trioxide dissolved with difficulty, and for that reason was not used.

Analytical methods for determining the various naphthol-sulfonic acids in mixtures were based on well-known industrial methods of selective coupling with diazonium compounds.[5] Thus the 6- and 8-isomers were determined by titrating the former with a molal solution of *p*-diazotoluene and continuing titration of the 8-sulfonic acid by coupling it with a p-nitro-diazobenzene solution. Simple mixtures of these two isomers could thus be analyzed with considerable accuracy. For sulfonation mixtures, however, which contained the l-sulfonic or the 1.6-disulfonic acid in addition, a few precautions had to be observed. These acids tended to combine with the more active diazonium compounds into peculiar addition products, highly soluble, but more unstable and of much lower color intensity than true azo dyes. Their formation could be practically eliminated by carrying out the titrations at low temperatures, between 0 and −5°, and especially by avoiding a high degree of alkalinity in the solution. No references for determining either the 1-sulfonic, or the 1.6-disulfonic acid in mixtures with other naphthol sulfonic acids appeared to be available, and a simple method therefore had to be devised. Fortunately, the sulfonic aci'd group in the 1-position may easily be eliminated by hydrolysis with acids at temperatures near the boiling point of water, and the resulting naphthol or naphthol-6-sulfonic acid may then be determined by the usual coupling methods. Sulfonic acid groups in the 6-, as well as in the 8-position, complete y resisted hydrolytic action of acids under the time and temperature conditions employed. Artificial mixtures of pure 6- and 1-sulfonic acids, and of 6-sulfonic and 1,6-disulfonic acid, could be determined with an accuracy of better than 1% by such a method.

Standard diazonium solutions were prepared by dissolving 0.1 mole of pure p-toluidine, or of *p*-nitro-aniline, respectively, in an excess of hydrochloric acid, and subsequent diazotization with the customary precautions. The solutions were diluted to one liter and standardized by titrating weighed amounts of pure naphthol dissolved in sodium hydroxide solution to which an excess of carbonate was added. Only freshly prepared diazonium solutions were used in titrations.

Procedure.—Sulfonations were carried out in Basks of 125-cc. capacity with a thermometer through an airtight stopper. Weighed amounts of sulfuric acid, or of sulfuric–boric acid mixture, were cooled below the intended equilibrium temperature, generally to about 10". Accurately weighed naphthol was placed in the flask in one addition and stirred into solution by means of the thermometer. Sulfonations at such lower temperatures proceeded slowly and could easily be controlled by occasional outside cooling. The temperature was allowed to rise gradually to the desired level, but never over. With boric acid present, sulfonation masses soon became extremely viscous and hardened after about thirty minutes' agitation, which was just sufficient to dissolve the finely divided naphthol. The flasks were tightly stoppered to prevent entrance of moisture and were partly immersed in a water-bath, which was maintained at a definite temperature, within one degree. Sulfonations over 35° were kept in an air-bath with automatic control, which maintained the desired temperature within two degrees. All experiments were made in duplicate. Procedure and analytical methods were varied as little as possible; representative experiments only need therefore be described.

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[5] Compare Fierz, "Farbenchemie," Zürich, 1920, pp. 296 ff.

2-Naphthol-1-sulfonic Acid

Experiment **Ia.**—A solution of 1.50 g. of metaboric acid in 30.0 g. of 100% sulfuric acid was cooled to 15°, and 14.40 g. of naphthol (0.1 mole) dissolved in it by vigorous stirring. Through outside cooling, the temperature was kept at 20 to 28° for the larger part of four minutes, the total duration of the reaction. At the end of this time, the naphthol had practically dissolved; the sulfonation mass was still fluid. Rapid dilution with ice and water arrested the reaction. The total volume of the diluted mass was brought up to 250 cc. exactly.

Unsulfonated naphthol, in suspension, was removed by filtration and the clear filtrate saved for subsequent determinations of sulfonated products. The recovered naphthol, properly washed, was dissolved in an equivalent amount of sodium hydroxide solution (thiazole indicator), and an excess of sodium carbonate added. Definite portions of the solution, one-fourth in this case, were titrated with 0.1 *M* p-diazotoluene hydrochloride solution, which required 68.6 and 68.7 cc., corresponding to a total of 0.0274 mole of unchanged naphthol. The remainder, 0.0726 mole, had therefore been sulfonated.

Naphthol-1-sulfonic acid was precipitated from the solution of sulfonated products by addition of sodium chloride, isolated and recrystallized. Its identity was established by its ferric chloride reaction (reddish blue coloration), the absence of fluorescence in alkaline solution, and by the ease with which it changed into naphthol and sulfuric acid on warming with dilute mineral acids. It coupled slowly, in the presence of alkali, with p-nitro-diazobenzene, yielding an oil-soluble, unsulfonated orange dye.

The solution of sulfonated products contained naphthol-6-sulfonic and traces of 8-sulfonic acids in amounts too small for isolation. These isomers were recognized by their behavior with diazonium compounds, the 6-sulfonic acid also by comparing the azo dye resulting through coupling with p-diazotoluene with a dye of known origin.

Analytical Determinations

Naphthol-6-sulfonic Acid.—One-fifth portions of the sulfonated products, 50 cc., were neutralized and an excess of sodium bicarbonate was added. The 6-sulfonic acid present required 12.6 and 12.8 cc. of 0.1 M p-diazotoluene hydrochloride solution, which corresponded to 63.5 cc. for the total solution. Of the sulfonated naphthol, 0.0064 mole or 8.8% had reacted to form 6-sulfonic acid.

Naphthol-1-sulfonic Acid.—A 50-cc. portion of sulfonation products was mixed with an equal volume of water and with 10 cc. of concd. hydrochloric acid, the solution gently refluxed for twenty minutes, then cooled and further diluted. Naphthol, produced through hydrolysis of the 1-sulfonic acid, was isolated by filtration, washed and determined by titration in an alkaline solution as described before. Two portions required 131.4 and 129.7 cc., respectively, of 0.1 M p-diazotoluene solution, equivalent to a total of 651 cc., or to 0.0651 mole of 1-sulfonic acid, or to 90% of the sulfonated naphthol.

Naphthol-8-sulfonic Acid.—The filtrate from the hydrolyzed naphthol was neutralized with an excess of sodium bicarbonate, the 6-sulfonic acid present titrated with 0.1 M p-diazotoluene solution, 12.4 and 12.5 cc. being consumed. This result was in good agreement with the previous determination in which original samples not subjected to hydrolysis had been used, which indicated that the naphthol-1,6-disulfonic acid could not have been formed to any extent during the short period of sulfonation. Naphthol-8-sulfonic acid was now determined by continuing the titration with 0.1 M *p*-nitrodiazobenzene solution, no more than **0.3** cc. being sufficient to reach an end-point—only a trace of the 8-sulfonic acid could have been present.

To summarize results, sulfonation under the conditions of the experiment had yielded mainly naphthol-1-sulfonic add, 90% of the sulfonated naphthol being thus accounted for. Small amounts of the 6-sulfonic (8.8%) and traces of the 8-sulfonic acids were formed besides. Parallel sulfonations gave closely similar results even though the amounts of naphthol actually sulfonated varied between 0.073 and 0.082 mole.

Practically Obtainable Yield of Naphthol-1-sulfonic Acid

Experiment Ic.—A solution of 3.00 g. of metaboric acid in 50.0 g. of 94.2% sulfuric acid was cooled to 15". Two-tenths mole of naphthol, 28.80 g., was stirred into the acid, the temperature of the mass being allowed to rise gradually to 25°. The naphthol solution, at first reddish brown, changed color, became extremely viscous, and hardened to a yellowish solid at the end of thirty minutes. The mass was kept at 28° for twenty-four hours. It was then dissolved, in small chips, in ice and water and the volume of the solution filled up to 250 cc. The naphthol had been sulfonated with the exception of a negligibly few larger particles. The yields of the reaction products were analytically determined—83% of the theoretically possible amount of 1-sulfonic, 3% of 6-sulfonic, 5% of 8-sulfonic and 9% of 1,6-disulfonic acids being found.

Isolation of **Naphthol-1-sulfonic** Acid.—One-half of the solution, which contained one-tenth mole of sulfonated naphthol, and 25 g. of sodium chloride were stirred together for twelve hours. The precipitated sodium salt of the 1-sulfonic acid was gathered on a suction funnel and repeatedly washed with small portions of saturated chloride solution, 125 cc. in all being used. The washed product contained a trace of mineral acid and gave a very faint reaction for 6-sulfonic acid with *p*-diazotoluene. For analytical determination, exactly one-tenth of the material, dissolved in 50 cc. of water and 15 cc. of concd. hydrochloric acid, was refluxed for twenty minutes, the liberated naphthol isolated and determined as usual. Two such portions, from exactly parallel sulfonation experiments, required 72.2 and 73.6 cc. of 0.1 M p-diazotoluene solution. The yield of *isolated,* useful product therefore corresponded to about 73% of the naphthol used.

2-Naphthol-1,6-disulfonic Acid

Experiment If.—Two-tenths mole of naphthol, or 28.80 g., was stirred into a solution of 3.00 g. of metaboric acid in 87.0 g. of 94.2% sulfuric acid. The temperature of the mixture was allowed to rise from 15°, at the beginning, to 30°. At the end of twenty minutes the mass solidified. It was maintained at 45° for thirty hours. In the process of disulfonation the material changed from a yellowish to a light gray coloration and softened a little. It was diluted with ice and water to a volume of exactly 250 cc. The analysis of test portions indicated the presence of small amounts of 6-sulfonic (4%) and of 8-sulfonic acids (24%). The main product of the reaction was the 1,6-disulfonic acid. Its dipotassium salt could be prepared in excellent yield and practically free from foreign admixtures in one operation by precipitating it with potassium acetate, and by washing the isolated material first with a 20% solution of acetate and then with ethyl alcohol to remove the acetate. A further recrystallization from water yielded crystals with one molecule of water, small slender prisms with a tendency to arrange in clusters. All faces appeared to be inclined at right angles toward each other, the crystals, presumably, possessing orthorhombic symmetry.

Anal. Calcd. for $C_{10}H_6O_7S_2K_2 \cdot H_2O$: S, 16.06; K, 19.63; H_2O, 4.52. Found: S, 15.98; K, 19.52; loss on drying at 90°, 4.47.

The disodium salt was precipitated from the solution of sulfonic acids with sodium chloride. It was isolated by filtration, washed with a saturated chloride solution to remove by-products and mineral acids and after complete neutralization recrystallized from hot water until free from chloride. It crystallized with three molecules of water and formed thin, elongated plates which had the characteristics of the triclinic system. Crystals of a centimeter's length could easily be produced.

Anal. Calcd. for $C_{10}H_6O_7S_2Na_2 \cdot 3H_2O$: S, 15.94; Na, 11.44; H_2O, 13.44. Found: S, 15.85; Na, 11.38; loss on drying at 70°, 13.55.

Properties and Constitution.—The disulfonic acid gave a clear, reddish blue coloration with ferric chloride solution. It did not form nitroso derivatives, nor was it capable of combining with diazobenzene, which appeared to indicate that one of the two sulfonic acid groups occupied the 1-position. Indeed, the more reactive nitrodiazobenzene coupled slowly, in the course of several hours, by displacing the obstructing sulfonic acid group. A monosulfonated orange dye and mineral sulfate resulted. The same sulfonic acid group could be removed through hydrolytic action of dilute mineral acids at 85 to 90°, the disulfonic acid reacting, in this respect, with the same ease as the naphthol-1-sulfonic acid, but quite unlike all the other known sulfonic acids (which hydrolyze at about 135°).

The product which remained after losing the mobile sulfonic acid group was found to be identical with 2-naphthol-6-sulfonic acid. It was recognized by comparing the azo dyes which resulted from coupling with diazobenzene and *p*-diazotoluene against dyes of known constitution. Its nitroso derivative, in conjunction with ferric chloride, yielded a characteristic green dye.[6] For further identification, the well-characterized free acid was prepared directly from the sulfonation products. These, it will be remembered, already contained a small amount of the 6-sulfonic acid. A somewhat quantitative as well as a qualitative determination of this product was therefore necessary.

One-tenth of the sulfonation products, 25 cc. of the solution, and 75 cc. of concd. hydrochloric acid, mixed, remained perfectly clear in the cold. After heating at 90°, for twenty minutes, a heavy precipitate, the 6-sulfonic acid, separated. It was collected on a suction filter and thoroughly washed with concd. hydrochloric acid until practically free from sulfuric acid. The crystals were redissolved in water and the solution was divided exactly in halves. One of these portions was saturated with hydrogen chloride, the reprecipitated product isolated and dried over technical potassium hydroxide sticks. The resulting material had the same composition and melting point (118") as the 2-naphthol-6-sulfonic acid $2H_2O$ prepared by Engel and Hutchison.[7] The monohydrate (m. p. 129") and the completely dehydrated material (m. p. 167°) were also obtained upon more vigorous drying.

The second portion of the 6-sulfonic acid solution (which originated from 0.01 mole of naphthol) was neutralized and titrated, in the presence of sodium bicarbonate, with 0.1 M p-diazotoluene solution. This required 64 cc., which corresponded to a recovery of 64% of the naphthol in the form of pure 6-sulfonic acid. With the exception of one-sixteenth, at the utmost, this quantity could have originated only through hydrolysis of the *2-naphthol-1,6-disulfonic acid.*

The ease with which this disulfonic acid hydrolyzed made a quantitative determination a simple task. One-twentieth of the sulfonation products, 12.5 cc. of the solution, was further diluted, neutralized and mixed with sodium bicarbonate. The 6-sulfonic acid, formed as a primary sulfonation product, consumed **4.3** and 4.2 cc. of 0.1 M *p*-diazotoluene solution. Another 12.5-cc. portion was mixed with 40 cc. of water and 10 cc. of concd. hydrochloric acid and the mixture gently refluxed for twenty minutes. After dilution, neutralization and addition of sodium bicarbonate, the 6-sulfonic acid now present required 76.3, 75.8 cc. of the p-diazotoluene solution. The difference between titrations before and after hydrolysis, 71.8 cc. in average, represented the

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[6] Society of Dyers and Colourists, "Colour Index," 1924, No. 5.

[7] K. H. Engel and A. W. Hutchison, THIS JOURNAL, 52, 211 (1930).

amount of 1,6-disulfonic acid originally in solution, and indicated a conversion of approximately 72% of the naphthol into this product.

Practically Obtainable Yield of **1,6-Disulfonic** Acid.—One-half of the sulfonation products, or 125 cc. of solution, and 25 g. of sodium chloride were stirred for twelve hours, a heavy, crystalline precipitate was isolated by filtration and washed with 125 cc. of saturated chloride solution. The disodium salt of the 1,6-disulfonic acid thus obtained was practically free from other sulfonation products. Portions of it were submitted to the hydrolytic action of dilute hydrochloric acid and the generated naphthol-6-sulfonic acid determined as before. This titration indicated a recovery of 64% of the naphthol in the form of the disodium salt of the 1,6-disulfonic acid.

Other Sulfonation Products.—Naphthol-6-sulfonic acid, formed in small amounts, could be isolated only in form of an azo dye obtained through coupling with *p*-diazotoluene. Dyeings upon wool or silk apparently agreed in shade and intensity with dyeings of a pure compound prepared from known intermediates and recrystallized from ethyl alcohol. An unsuccessful search was made for very small amounts of the unknown 2-naphthol-3-sulfonic acid.

Naphthol-8-sulfonic acid, although formed in appreciable amounts, likewise resisted isolation on account of the extreme solubility of its metal salts. It also was changed into an azo dye. A portion of the sulfonation products was titrated with P-diazotoluene solution until all 6-sulfonic acid present had combined. The resulting scarlet dye was precipitated with sodium chloride and removed by filtration. The weakly colored filtrate, which contained the 8-sulfonic acid, was mixed with its exact equivalent of diazobenzene hydrochloride solution; all combinations, of course, were carried out in the presence of sodium bicarbonate and at the freezing point. The precipitated orange dye was isolated and dried. It showed pronounced solubility in ethyl alcohol, and separated from a hot saturated solution in well-formed slender prisms which were obliquely cut and belonged, apparently, to the monoclinic system. The product agreed in all characteristics with a dye prepared from a known sample of 8-sulfonic acid.

The 2-naphthol-8-sulfonic acid was quantitatively determined by titration with 0.1 M *p*-nitrodiazobenzene solution.

Sulfonations under varying conditions were investigated in a similar manner as described in the preceding pages. Wherever the actual quantities of reaction product were small, their isolation was not attempted.

Summary

The presence of boric acid during sulfonations of 2-naphthol caused no changes in the familiar substitution tendencies of the naphthol, but influenced the yield ratios of commonly concurring reaction products decidedly.

Its presence favored the retention of the loosely held 1-sulfonic acid group in the naphthol-1-sulfonic and the 1,6-disulfonic acids.

The same disulfonic acid was found to be a by-product of ordinary, straight sulfonations at temperatures up to 75°. It formed the main reaction product in sulfonations under 18°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE PREPARATION OF 2-ALKYL AND 2-ARYL PYRIDINES AND QUINOLINES BY THE GRIGNARD REACTION[1] (PRELIMINARY)

BY F. W. BERGSTROM AND S. H. MCALLISTER

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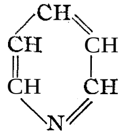
Introduction

Franklin and Strain[2] have pointed out, as a logical result of the known similarities between water and ammonia, that substances containing the grouping —CH=N— may be regarded as aldehydes of an ammonia system, comparable with aldehydes of the water system, which contain the analogous grouping, —CHO. The Schiff bases, of which benzalaniline, $C_6H_5CH=NC_6H_5$, is the simplest aromatic representative, are thus found to possess very distinct aldehydic properties.[3]

If the Korner formula of pyridine, , is correct—or potentially so--there is present the same—CH=N—group that occurs in the Schiff bases and is characteristic of aldehydes of the ammonia system. Furthermore, pyridine and all substances containing a pyridine nucleus also partake of the nature of acetals, since one valence of the nitrogen is attached to one side of a closed ring. Hence pyridine, quinoline and isoquinoline can be regarded in a formal sense as cyclic ammono aldehyde acetals.[4] Nevertheless, the aldehydic properties one might expect these substances to show are subordinated because of the remarkable stability of the six-membered ring with alternate double and single bonds.[5] Thus, pyridine is not appreciably oxidized by hot concentrated sulfuric or nitric acid. Quinoline may be oxidized to quinolinic acid by potassium permanganate in alkaline solution with the destruction of the benzene ring.

However, if the stability of the pyridine ring of quinoline be diminished by the destruction of one of the double bonds in this ring, the aldehydic character of the molecule becomes pronounced. The rupture of this

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[1] A portion of the theory was presented by one of us (F. W. B.) at the Swampscott meeting of the American Chemical Society, September, 1928, and at the Pomona meeting of the American Association for the Advancement of Science, June, 1928 (with H. M. Leicester and D. N. Benton).

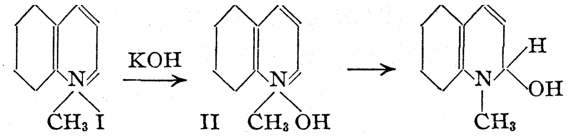
[2] (a) Franklin, THIS JOURNAL, 46, 2153 (1924); (b) Strain, *ibid.*, 49, 1558 (1927).

[3] Ref. 2b, p. 1559; Busch, *Ber.*, 37, 2691 (1904); *ibid.*, **38**, 1761 (1905); Miller and Plochl, *ibid.*, 25, 2020 (1892).

[4] A substance which combines in this manner the characteristics of an aldehyde and of an acetal is unknown in the water system, because oxygen is divalent while nitrogen is trivalent.

[5] Compare the difference in properties between the stable and relatively saturated benzene and the typically unsaturated cyclohexadiene.

double bond may be accomplished by adding methyl alcohol to the —CH=N— group of quinoline, in accordance with the equation[e]



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Since this process, in so far as the final results are concerned, is clearly analogous to the addition of alcohol to chloral to form chloral alcoholate, we can look upon III, 1-methyl-2-hydroxy-1,2-dihydroquinoline, as an aldehyde alcoholate related at the same time to the water and ammonia systems. The 1-alkyl-2-hydroxy-1,2-dihydroquinolines, like the aldehyde alcoholates, undergo many aldehydic reaction with ease.[6] Because of this it is not unreasonable to believe that several reactions of pyridine, quinoline and isoquinoline themselves may have their counterpart in corresponding reactions of the familiar aquo aldehydes. Thus, Oddo[7] found that 2-phenylquinoline was formed by heating quinoline, or a mixture of quinoline and pyridine with benzene, phenyl bromide and magnesium. Since he was not primarily concerned with the preparation of 2-aryl quinolines, and since his yield of 2-phenylquinoline was undoubtedly low, it was thought worth while to repeat his experiments and to extend them in an attempt to prepare other alkyl pyridines and quinolines. Such an investigation, if successful, would support the view that the —CH=N— group is aldehydic in character, or potentially so, even though it may be present in a stable six-membered ring.

Preliminary Experiments

A number of attempts were made to obtain 2-phenylquinoline by heating quinoline for about two hours with solutions of an excess of phenylmagnesium bromide in boiling diethyl ether, benzene, toluene, xylene or diamyl ether.[8,9] In diethyl ether no reaction occurred other than the formation of the known addition compound,[10] which yields unchanged quinoline on hydrolysis. Large quantities of a viscous tar were formed in the other solvents, together with small amounts of 2-phenylquinoline. Much better results were obtained by autoclaving pyridine, quinoline or isoquinoline with the Grignard reagent in diethyl ether solution at 150–160°.

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[6] (a) Decker, *Ber.*, **25**, 443, 3326 (1892); Decker and Becker, *Ann.*, **395**, 374 (1913); (b) Decker and Kaufmann, *J. prakt. Chem.*, *84*, [*N.* F.] 241 (1911).

[7] Oddo, *Atti accad. Lincei*, [V] **16**, 538 (1907).

[8] The diamyl ether was presented to us by the Sharples Solvents Corporation.

[9] Gilman, Kirby and Kinney have recently added the Grignard reagent under forced conditions to the —CH=N— group of certain Schiff bases in toluene solution [THIS JOURNAL, **51**, 2252 (1929)]. This addition often takes place without forcing. See Busch, Ref. 3.

[10] Sachs and Sachs, *Ber.*, **37**, 3088 (1904); Oddo. Ref. 7.

The Reaction of Pyridine, Quinoline and Isoquinoline with the Grignard Reagent

The autoclave in which the reactions were carried out was made from a two-foot length of seamless steel tubing, two inches in internal diameter. Into one end was welded a steel plug which took externally the form of an hexagonal nut. The hexagonal screwed top of the autoclave was jacketed and water-cooled for the purpose of keeping the lead gasket in the head cool and thus insuring absolute tightness. The general method of preparing 2-alkyl or 2-aryl pyridines and quinolines may best be illustrated by the preparation of 2-phenylquinoline.

Yhenylmagnesium bromide was prepared in the usual manner from 78 g. of phenylbromide, 150 cc. of anhydrous diethyl ether and an excess of magnesium shavings in a pyrex tube fitting snugly into the interior of the autoclave.. To this solution was added 52 g. of quinoline in 100 cc. of ether. A white flocculent precipitate of the addition compound of quinoline and phenylmagnesium bromide was formed. The space in the pyrex tube above the ether solution was filled with nitrogen, the tube placed in the autoclave and the head screwed on while the hexagonal nut at the bottom was held in a suitable vise. The autoclave was heated over its full length in an upright electric furnace for three hours at 150-160° (temperature of the furnace). The ethereal solution after heating was a dark red and the reaction vessel contained some ether-insoluble tar. The Grignard addition compound was decomposed with an aqueous solution of ammonium chloride. During this decomposition hydrogen was given off, but in much less than the expected quantity. The ether layer was separated, the water was extracted with an additional quantity of ether and the combined ethereal solutions distilled. The 2-phenylquinoline was contained in the portion boiling between 310 and 330" at atmospheric pressure. The solidified distillate after one crystallization from 70% alcohol weighed 55 g., melted at 78.5° and was therefore crude 2-phenylquinoline, which melts when pure at 83.5". Light yellow needles having this melting point were obtained after several crystallizations from 70% alcohol. The mixed melting point of this product with known 2-phenylquinoline prepared from cinnamic aldehyde and aniline[10a] was 83.5"; yield of the crude product, 66%.

The yield of 2-phenylquinoline was diminished if too small a quantity of solvent ether was used or if the particles of unused magnesium were allowed to remain in the reaction vessel. In some experiments, therefore, magnesium in a copper basket was suspended in the ethereal solution of the alkyl or aryl halide, the basket being withdrawn together with the unchanged magnesium, after the formation of the Grignard reagent.

In the following experiments a solution of 30–40% excess of the appropriate Grignard reagent in about 150 cc. of anhydrous ether was heated with pyridine or isoquinoline for three hours at 150–160°. A smaller autoclave about one inch in internal diameter served as pressure vessel. The ethereal solutions after heating were colored a dark red or violet and some tar was found in the bottom of the reaction tube. This mixture was hydrolyzed with an aqueous solution of ammonium chloride, the ethereal layer and the ethereal extracts of the aqueous phase were distilled and the fraction of proper boiling point was saved as the product.

2-Phenylpyridine was prepared in 44% yield from 43 g. of phenyl bromide[11] and 16 g. of pyridine; b. p. 270-272° at 760 mm., uncorr.; m. p. of picrate, 169–170°, un-

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[10a] Grimaux, Compt. rend., 96, 584 (1883).

[11] An excess of magnesium was used in the formation of the Grignard reagent to avoid the presence of free phenyl bromide or ethyl bromide.

corr. (m. p. given in literature, 169–170" uncorr.); nitrogen in the picrate, Dumas, 14.6. Calcd. for $C_{17}H_{12}N_4O_7$: N, 14.5.

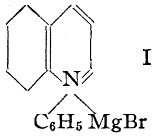
2-Ethylpyridine was prepared in 45% yield from 30 g. of ethyl bromide[11] and 16 g. of pyridine; b. p. 148–150° at 760 mm. The picrate melted at 187–189°, uncorr. Nitrogen in the picrate, Dumas, 16.5. Calcd. for $C_{13}H_{12}N_4O_7$: N, 16.6. Gold chloride double salt, m. p. 120° (m. p. 120°, according to the literature); yield, 45% of the theoretical.

1-Ethylisoquinoline.—B. p. 250°, uncorr., at 760 mm.; light yellow oil of pleasant odor, insoluble in water, but soluble in ether and alcohol; heavier than water; m. p. of picrate, 207 210°, uncorr.; m. p. of $PtCl_4$ double salt, 199–200°, uncorr.; m. p. of gold chloride double salt, 168–172°, uncorr. Calcd. for $C_{11}H_{11}N{\cdot}HCl{\cdot}AuCl_3$: Au, 36.6. Found: Au, 40.0. 0.1801 g. of the free base gave 14.2 cc. of nitrogen at 21.5" and 765 mm.; 0 2008 g. gave 16.9 cc. of nitrogen at 25.5° and 765 mm. (Dumas). Nitrogen: 9.0, 9.4. Calcd. for $C_{11}H_{11}N$: N, 9 0. Since the melting point of 3-ethylisoquinoline picrate is 171–173°, of 3-ethylisoquinoline gold chloride is 115–117°, and since 4-ethylisoquinoline is a solid melting at 62°, the present preparation must be 1-ethylisoquinoline; yield, 66% of the theoretical [from 32 g. of ethyl bromide[11] and 28 g. of isoquinoline].

Other Reactions.—Ethylmagnesium bromide reacts with nicotine and cinchonine in diethyl ether at 150°. The products of the reaction with cinchonine are a trifle tarry and have not as yet been identified. Nicotine appears to be converted in some measure to an ethylnicotine, but there is a simultaneous reduction to a base having a piperidine-like odor. 2-Picoline and quinaldine also react with ethylmagnesium bromide under the same conditions, but the products have not been definitely identified. The product of the reaction of 4,4′-dipyridyl, a dicyclic ammono dialdehyde-acetal, and ethylmagnesium bromide in diamyl ether solution at 160" is largely a tar. 2-Phenyl pyridine and 2-ethyl pyridine were formed in poor yield in diamyl ether solution at 150".

Discussion

In all of the reactions described in this paper, the Grignard reagent first forms with pyridine, quinoline or isoquinoline a precipitate of an addition compound that is only sparingly soluble in ether. These addition compounds[10] are supposed to have the structure of a substituted ammonium salt I. Under the influence of heat, the phenyl group of I migrates to the adjacent carbon atom to give II. As a net result the Grignard reagent has been added to the potentially aldehydic —CH=N— group in the expected manner, that is, with the —MgBr group seeking the nitrogen just as it seeks the oxygen of an aquo aldehyde. The conversion of II into 2-phenylquinoline probably takes the course



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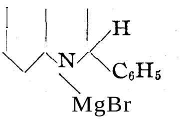
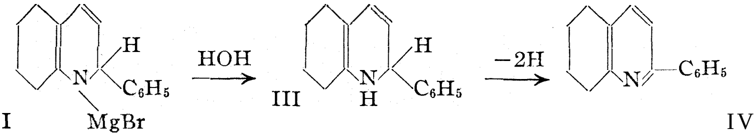


II



The loss of hydrogen from compound III finds its counterpart in the loss of hydrogen from the dihydroquinolines that probably appear as intermediate products in the Dobner–Miller quinaldine synthesis.[12] The dihydropyri-

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[12] Ddbner and Miller. *Ber.*, 16, 2465 (1883).

dines resulting from the action of ammonia on aldehydes likewise lose hydrogen and pass into the corresponding pyridines.[13] The hydrogen resulting from the conversion of III into IV above always fell considerably below the amount theoretically expected. Perhaps some of this hydrogen was utilized in forming reduction products, and some of the dihydro bases (III) may have been polymerized to a tar, without loss of hydrogen.

β- and γ-substituted pyridines and quinolines were not isolated in the present work, although it is posible that they are formed in small quantity. The migration of the alkyl or aryl group of formula I from nitrogen to the 2-carbon then does not strictly follow the migration of an alkyl group from nitrogen to the 2 and 4 carbons in the Ladenburg synthesis of alkyl pyridines and quinolines.[14]

Summary

1. Pyridine, quinoline and isoquinoline react with the Grignard reagent in diethyl ether solution at 150–160° to form a-alkyl or aryl pyridines, quinolines or isoquinolines in yields varying between 44 and 66% of the theoretical.

2. The following compounds have been prepared: 2-ethylpyridine, 2-phenylpyridine, 2-phenylquinoline and 1-ethylisoquinoline. 1-Ethylisoquinoline has been prepared for the first time.

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[CONTRIBUTION FROM THE LABORATORIUM FUER CHEMISCHE TECHNOLOGIE DER UNIVERSITAET WIEN, VIENNA, AUSTRIA, AND NORTHWESTERN UNIVERSITY, MEDICAL SCHOOL, DEPARTMENT OF RESEARCH BACTERIOLOGY, CHICAGO, ILLINOIS]

CELLULOSE SULFONIC ACID ESTER

BY E. GEBAUER-FUELNEGG AND OTTO DINGLER

RECEIVED JANUARY 29, 1930 PUBLISHED JULY 3, 1930

In a preliminary report[1] the formation of a trisulfonic acid ester derived from cellulose was reported. This compound was obtained by the action of chlorosulfonic acid in an excess of pyridine on cellulose (pure filter paper or cotton). Data were given as to its formation, general properties and analysis.[2] It was found that films and threads can be formed from this ester and its salts.

[13] Chichibabin, J. prakt. Chem., 107, [N. F.] 122 (1924).

[14] Ladenburg, *Ber.*, **32,** 42 (1899); 16, 1410, 2059 (1883)

[1] Gebauer-Fuelnegg, Stevens and Dingler, *ibid.*, 61, 2000 (1928).

[2] In the first report the statement has been made that a second treatment of cellulose-trisulfonic acid ester with the pyridine chlorosulfonic acid reagent will give a purer substance and complete the triesterification. We were unable to repeat the results of the respective preliminary experiments, from which the figures have been taken. On the contrary, it was found that under certain circumstances one SO_3H group is eliminated by this procedure. We will report on this reaction later.

It was pointed out that the pyridine salt of the ester did not show rotation in aqueous solution, nor did it reduce Fehling's solution, and contrasted in these properties appreciably with a cellulose sulfonic acid ester prepared recently by Traube and co-workers.[3] These authors prepared the ester by the action of sulfur trioxide on well-dried cotton. There are, however, certain similarities between the two cellulose sulfonic acid esters.

The ester obtained by Traube and co-workers is stated to be a derivative of undegraded cellulose. As to the structure of the ester obtained by the action of the pyridine-chlorosulfonic acid reagent on cellulose, however, we have considered three possibilities. (I) The product might be a derivative of undegraded cellulose, an assumption supported by the fact that no rotation or reduction of Fehling's solution could be observed. (II) The ester might be a degradation product of cellulose. (III) It might be a degradation product of cellulose which on further action of the pyridine-chlorosulfonic acid reagent repolymerized to form a cellulose-like carbohydrate.

In the first paper it was stated that even though equality in fundamental properties such as reducing power and rotation would be expected if both products were derived from undegraded cellulose, the differences actually observed could be ascribed to the different preparational methods, according to ideas recently developed by Kurt H. Meyer and H. Mark.[4]

To determine whether or not our ester is a derivative of undegraded cellulose, hydrolysis of the sulfonic group was attempted with various agents. It was found that the trisulfonic acid ester mentioned showed the same resistance to splitting of the ester group as did the ester described by Traube. In fact, the latter author failed to find a suitable method for hydrolysis of his preparation.

A large variety of hydrolyzing agents was tried, such as ammonia, alkalies of various concentrations, alkyl amines and water, but no appreciable effect was noticed. Even dilute acids did not change the compound materially; concentrated hydrochloric acid only was found to split off the SO_3H groups, but intense degradation was observed with this reaction, as would be expected. Finally, methyl alcoholic hydrochloric acid (0.25–1%) was found to be a suitable hydrolyzing agent at 100–120°. In the course of the work it was found that boiling with methyl alcohol containing 5% of hydrogen chloride gas for a few hours also effected the hydrolysis.

The product obtained was a sulfur and nitrogen (pyridine) free white powder soluble only in cellulose solvents such as ammoniacal copper oxide, from which it could be precipitated without chemical changes.

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[3] Traube and co-workers. *Ber.*, 61, 754 (1928).

[4] Meyer and Mark, *ibid.*, 61, 610 (1928).

A small methoxyl content was detected, apparently due to the methylating action of the methyl alcoholic hydrochloric acid.

The rotation values of the ammoniacal copper oxide solutions showed the presence of chemically unchanged (but hydrated) cellulose and were comparable with parallel tests made with native cellulose.

Even though the results of this hydrolysis clearly showed that the sulfonic acid ester obtained by the pyridine-chlorosulfonic acid reagent was a true derivative of cellulose, an attempt was made to convert the product of hydrolysis, by acetylation and methylation, into definite cellulose derivatives of known properties. A direct exchange of the sulfonic groups of the original ester with methyl or acetyl groups also was attempted.

Acetylation and methylation of the hydrolysis product were found to be successful, while the direct exchange of the SO_3H groups of the original ester did not yield definite compounds.

The product of acetylation was triacetylcellulose, the rotatory power of which was found to be the same as that given for the triacetyl derivative of native cellulose.

Methylation also was finally accomplished, but some difficulties were encountered. There are methods for permethylation of cellulose described by Irvine,[5] Hess and Pichelmayer[6] and Urban and Freudenberg.[7] In order to find the most suitable method for the product in question, preliminary experiments were carried out with regenerated cellulose of other (known) origin, but with some relation as to the preparational method and general appearance of the substance in question. Hydrolysis of triacetylcellulose prepared with acetic anhydride and sulfuric acid, it was thought, would give such a related cellulose upon hydrolysis, since the cellulose regenerated is reported to be insoluble in alkali as is the cellulose regenerated from the trisulfonic acid ester. Accordingly this was used in the preliminary work.

The methylation method of Hess and Pichelmayer therefore at first was thought not to be suitable since it is used with alkali-soluble cellulose. The method of Urban and Freudenberg also was found to be unsatisfactory for this purpose. Even on increasing the amount of reagent and repeating the procedure, products of low methoxy content were obtained. Finally, the procedure given by Hess and Pichelmayer actually was used with good results. After nine successive methylations a trimethylcellulose with 43% methoxyl was obtained.

As expected, this method was found to be suitable for the methylation of the cellulose regenerated from the trisulfonic acid ester; the trimethyl-

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[5] Irvine, **J.** *Chem. Soc.*, **123,** *529* (1923).

[6] Hess and Pichelmayer. *Ann.*, 450, **31** (1926).

[7] Urban and Freudenberg, *Cellulosechemie*, 7, **73** (1926).

cellulose obtained was found to be identical with the trimethylcellulose described by Hess and co-workers. It might be added that the solubility in water of the trimethylcellulose from cellulosetrisulfonate is practically negligible. It is known that trimethylcelluloses are increasingly soluble in water with increasing degree of depolymerization, derivatives of native cellulose being less soluble than preparations from slightly degraded cellulose. This fact is a further indication that the cellulose trisulfonic acid ester is a derivative of coniparatively slightly degraded hydrated cellulose.

Experimental Part

Attempts to Hydrolyze the **Pyridine** Salt of the Cellulose Trisulfonate.—The pyridine salt of the cellulose trisulfonate is prepared by adding **3** g. of carefully dried cotton to a mixture of 11.6 g. of chlorosulfonic acid and 27 4 g. of pyridine (care!) and heating the reaction mixture on the water-bath for one hour. Swelling of the cellulose is noticed first and a sirupy, viscous mass is finally obtained. The mixture is cooled and water is added, from which the ester salt is precipitated, for example, with alcohol. This is repeated several times. Details of procedure and constitution of the reagent are given in the earlier report.'

(a) No hydrolysis could be effected on shaking the pyridine salt with an excess of water for three days, nor by boiling under reflux for eight days.

(b) With $N/50$, $N/10$, $N/2$ and 2 N potassium hydroxide no hydrolysis of the SO_3H groups could be effected, either on the shaking machine or on boiling under reflux.

(c) Aqueous hydrochloric acid of various higher concentrations was found to effect the splitting of the SO_3H groups on boiling, but its use resulted in a degradation of the cellulose part of the substance.

(d) Finally the hydrolysis was accomplished with methyl alcoholic hydrochloric acid. The best results for this type of hydrolysis of the above salt were obtained by heating a sample with absolute methyl alcohol containing 0.25% of dry hydrogen chloride gas in an autoclave at 110". A dark, clear, pyridine-containing liquid and a white powder were obtained. The liquid gave a sulfate reaction and a strong reduction of Fehling's solution; a small amount of an osazone could be precipitated, indicating the presence of sugars. The residue was washed with water (negative test for sulfate). A determination of the methoxyl groups gave the following results: subs., 6.475 mg.: AgI, 0.799 mg. Found: OCH_3, 1.63.

This product was white, contained no nitrogen or sulfur, was insoluble in water but was soluble, however, in hot 2 N potassium hydroxide and in cuprammine solution. It was possible to dye it with substantive dyes in the same shade and fastness as cotton.

(e) The most convenient method of hydrolyzing the SO_3H groups was the following: 50 g. of ester salt was boiled under reflux for six hours with 200 cc. of methyl alcohol to which 5% of concd. aqueous hydrochloric acid was added. After filtration of the brownish-yellow pyridine sulfate-containing liquid, the residue was extracted in a Soxhlet apparatus with boiling water until no sulfate could be detected. It was then washed with alcohol and ether. Only a very small portion of the product thus obtained was found to be soluble in hot strong potassium hydroxide and precipitable from it with acids. After drying it at 100° the product was found to have lost its solubility in alkalies. It is, however, easily soluble in cuprammine solution. The specific rotation was determined with the light of so-called "Effektkohlen"for blue light.

Hydrolyzed product (1.2991 g.) was placed in a 100-cc. volumetric flask, mixed with 1.3522 g. of copper hydroxide prepared according to the method of J. Habermann,[8]

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[8] Habermann, Z. *anorg. Chem..* 50, 318 (1906).

wetted with concd. ammonia and diluted to the mark of the flask. A slight turbidity could not be removed either by filtration or by centrifuging the solution. In order to obtain comparable results a parallel run was made with native cellulose (cotton). The product of hydrolysis showed: $\alpha = 7.50°$; cotton, $\alpha = 6.75''$; methoxyl content of product of hydrolysis, traces only.

Acetylation of the Product of Hydrolysis.—In parallel runs 20 g. each of the above product of hydrolysis (prepared according to Procedure (e)) and cotton was heated at 30° for eight hours with 75 cc. of glacial acetic acid, 75 cc. of acetic anhydride and 2 cc. of concd. sulfuric acid. Since the product of the above hydrolysis was not entirely dissolved, both mixtures were treated for sixteen hours more. They were filtered through a glass filter. The solution obtained from the native cotton was found to be more viscous than the product obtained from the regenerated cellulose. The acetylcellulose was separated in the ordinary way by precipitation in water, filtration, drying in a desiccator and purification by dissolving in chloroform and precipitating with ether.

The yields of crude products were 90% obtained from cotton and 81% from regenerated cellulose.

$$\text{Triacetate from cotton } \left[\alpha\right]_{D}^{16} = \frac{0.64°}{2 \text{ X } 1.4780} = -21.65° \text{ (CHCl}_3\text{)}$$

$$\text{Triacetate from regenerated cellulose } \left[\alpha\right]_{D}^{16} = \frac{100 \times 0.54°}{2 \times 1.2431} = -21.72'' \text{ (Chloroform)}$$

Both triacetates were hydrolyzed according to the procedure given by Hess[9] with methyl alcoholic sodium hydroxide and found to yield identical products, as expected.

Methylation.—Ten grams each of the above products of hydrolysis (from native cellulose-triacetate and from the triacetate obtained from hydrolyzed cellulose trisulfonate) were powdered and treated for several days with 20 cc. of potassium hydroxide (1:1); 80 cc. of water was added and methylation was accomplished with dimethyl sulfate according to the method of Hess and Pichelmayer.[6] The reaction was carried out at 55–60" in nine successive steps. The dimethyl sulfate was added drop by drop, with efficient stirring, as indicated in Table I.

TABLE I

PREPARATIONAL DATA

Steps	H_2O, cc.	NaOH, g.	$(CH_3)_2SO_4$, cc.	Minutes	Steps	H_2O, cc.	NaOH, g.	$(CH_3)_2SO_4$, cc.	Minutes
I	100	10	5	10	IV	..	50	..	10
II	...	15		10		..	..	10	10
			5	10				10	10
			5	10		..	..	..	30
	...	..		30	V	100	100	40	180
III	...	20		10	VI	75	125	20	180
	...	..	5	10	VII	25	50	10	180
			5	10	VIII	25	50	10	180
				30	IX	25	50	10	180

The first isolation of the reaction product was accomplished after the fifth step, by washing the mixture on a hot-water funnel with boiling water until freed from sulfate. For the next methylation the residue was transferred to the reaction flask with the proper amount of ice water. After the seventh step the product obtained was slightly soluble in benzene. The ninth methylation yielded a substance almost entirely soluble in benzene. Purification was accomplished by repeatedly dissolving the product

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[9] Kurt Hess, "Chemie der Cellulose und ihrer Begleiter," page 415.

in benzene and precipitating it with ligroin. The fractional extraction with ice water as given by Hess and Pichelmayer was found to be superfluous since the products in both cases were found to be insoluble. After the reprecipitation the product was treated with ether and finally dried in a vacuum to constant weight. The analyses prove the presence of a trimethylated product.

Anal. Subs., 4.552 mg.: CO_2, 8.734 mg.; H_2O, 3.211. Subs., 4.309 mg.: AgI, 13.794 mg. Subs., 0.1177: CO_2, 0.2278; H_2O, 0.0840. Subs., 0.1528: AgI, 0.5177. Calcd. for $C_6H_7O_5(CH_3)_3$: C, 52.91; H, 7.90; OCH_3, 45.50. Found: (on crude product before reprecipitation) C, 52.34; H, 7.89; OCH_3, 42.29; (pure product) C, 52.80; H, 7.99; OCH_3, 44.77.

The rotation of the trimethylcellulose obtained by the hydrolysis of cellulose trisulfonate was

$$\left[\alpha\right]_D^{21} = \frac{0.18^\circ}{1 \times 0.9751} = -18.46' \text{ (benzene)}$$

The rotation of trimethylcellulose obtained by the hydrolysis of triacetylcellulose was

$$\left[\alpha\right]_D^{21} = \frac{100 \times 0\ 21^\circ}{1 \times 1.1302} = -18.58^\circ \text{ (benzene)}$$

Summary

To determine whether a trisulfonic acid ester obtained from cellulose by the action of a pyridine-chlorosulfonic acid reagent on cellulose was (I) a derivative of undegraded or very slightly degraded cellulose, (2) a degradation product or **(3)** a repolymerized degradation product, it was hydrolyzed by means of methyl alcoholic hydrochloric acid. The sulfur-free product of hydrolysis showed (in cuprammine solution) a rotation of the order of magnitude given for native cellulose. Even though this was already a fairly good proof that the original ester was a true derivative of cellulose, this product of hydrolysis was converted to trimethyl- and triacetylcellulose. The products obtained were found to be most closely related to known preparations from native cellulose. The direct conversion of the cellulose trisulfonic acid ester into trimethyl- or triacetylcellulose could not be accomplished.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE PH-STABILITY REGIONS OF SERUM ALBUMIN AND OF SERUM GLOBULIN

BY THE SVEDBERG AND BERTIL SJÖGREN

RECEIVED JANUARY 30, 1930 PUBLISHED JULY 3, 1930

In a previous communication[1] a report has been given of the determination by ultracentrifugal methods of the molecular weights of serum albumin and serum globulin at their isoelectric points. It was found that both these proteins when isolated in an appropriate manner are homogeneous with regard to molecular weight. Serum albumin gave the value 67,500 ± 2000 and serum globulin 103,800 ± 3000. For serum albumin the sedimentation constant at 20° is 4.21×10^{-13} and for serum globulin 5.66×10^{-13}. The corresponding diffusion constants are 6.10×10^{-7} and 5.41×10^{-7}. Serum albumin has practically the same molecular weight, the same sedimentation constant and the same diffusion constant as hemoglobin, while serum globulin resembles as regards these constants r-phycocyan at a *P*H of 6.8. A few preliminary experiments were performed in order to determine the molecular weights of the products obtained from serum globulin by fractional precipitation, *viz.*, the so-called euglobulins and pseudoglobulins. The data obtained seemed to indicate that the originally homogeneous globulin was partially decomposed during the process of fractionation. It was therefore concluded that euglobulin and pseudoglobulin most probably represent artificial products not originally present in the blood serum.

The eminent importance of the serum proteins makes it desirable to extend the determination of their molecular weights to a wider range of *P*H and also to study more thoroughly the question of the homogeneity of serum globulin.

Preparation of Material.—The protein material was prepared from horse blood. Serum albumin was isolated from the serum as described under the head "serum albumin II" of the previous communication. The stock solution which served for the determinations in the middle PH region was kept at a PH of 4.8 (0.008 M in acetic acid and 0.012 M in sodium acetate). The stock solution for determinations in extreme acid and extreme alkaline solutions was kept in electrolyte-free condition.

Serum globulin was isolated from the serum as described under the head "serum globulin II" of the previous communication. The main part of the stock solution was kept at a PH of 5.5 (0.19 M in KH_2PO_4 and 0.009 M in Na_2HPO_4). For the determinations on the acid side of the isoelectric point a stock solution was prepared in the following way. The material was precipitated three times with ammonium sulfate, as before, dissolved in acetate buffer of PH 4.6 (0.1 M in acetic acid and 0.1 M in sodium acetate), and dialyzed against the same buffer until the outer liquid was free from sulfate and chloride.

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[1] T. Svedberg and B. Sjögren, THIS JOURNAL, 50, 3318 (1928).

Pseudoglobulin and euglobulin were prepared from the serum globulin stock solution by dialyzing at 5° for a week against distilled water saturated with toluene. After this treatment, followed electrodialysis with a current density of 0.5 milliampere per sq. cm. for thirty-six hours. After filtering, the pseudoglobulin solution was brought to a PH of 5.5 by making it 0.019 M in KH_2PO_4 and 0.001 M in Na_2HPO_4. The euglobulin precipitate formed during the dialysis and the electrodialysis was washed with distilled water, saturated with toluene until the filtrate was found to be free from protein and then dissolved completely in phosphate buffer of PH 5.5 (0.19 M in KH_2PO_4 and 0.009 M in Na_2HPO_4) and dialyzed against the same buffer for a week.

Light Absorption.—The measurements were made with the Judd–Lewis spectrophotometer in 20 mm. cells. Serum albumin was measured in 0.10% solution, serum globulin, pseudoglobulin and euglobulin in 0.05 and 0.10% solutions. In Tables I and II the data for serum albumin and serum globulin are given.

TABLE I

LIGHT ABSORPTION OF SOLUTIONS OF SERUM ALBUMIN

Solvent				PH of soln.	Wave length of maximum in $\mu\mu$	Wave length of minimum in $\mu\mu$	Extinction coeff ϵ/c of max
Subs.	M	Subs.	M				
HCl	0.046	KCl	0.054	1.4	278	250	5 0
HCl	.007	KCl	.093	2.2	278	254	4 8
HAc	.018	NaAc	.002	3.6	280	252	4 8
Na_2HPO_4	.032	NaOH	,002	9.4	278	250	5 2
Na_2HPO_4	.026	NaOH	.012	10.4	278	252	7 4

TABLE II

LIGHT ABSORPTION OF SOLUTIONS OF SERUM GLOBULIN

Solvent				PH of soln.	Wave length of maximum in $\mu\mu$	Wave length of minimum in $\mu\mu$	Extinction coeff. ϵ/c of max.
Subs.	M	Subs.	M				
HCl	0.072	KCl	0.005	1.3	285	255	18.0
HAc	.023	NaAc	.023				
HCl	.025	KCl	.025	2.5	280	255	18.5
HAc	.023	NaAc	.023				
NaOH	.023						
KH_2PO_4	.026	Na_2HPO_4	.174	7.5	284	254	18.5
KH_2PO_4	.002	Na_2HPO_4	.003	12.5	282	253	23.0
NaOH	.048	NaCl	1%				

The measurements show that within the limits of error the position of the maximum and the minimum does not change with PH. The extinction at the maximum is independent of PH except at high alkalinity, where it increases slightly for serum albumin as well as for serum globulin. In the previous communication the maximum extinction coefficient of isoelectric serum globulin was found to be 22. The lower value of 18 now found is probably due to difference in the protein material. A slight change in the chemical composition would in all probability not affect the molecular weight but might very well make itself visible in the light absorption. The study of the sedimentation constant has shown that the serum albumin molecule is stable within the PH region 4.0–9.0 and the serum globulin molecule in the region 4.0–8.0. The sedimentation equilibrium determinations indicate that the first stage in the decomposition of both these proteins consists in the disintegration into submolecules of approximately the mass one-half of the original molecule in the case of serum albumin and probably one-third in the case of serum globulin. This disintegration (being proved to be reversible) will in all probability not affect the chemical or optical properties of the protein very much and this accounts for the constancy of the light absorption. It is of interest to compare this behavior of the serum proteins with that of Bence-Jones protein.[2] In the case of this latter protein the first stage in the decomposition consists in the breaking down of the protein unit itself and this is accompanied by a strong increase in light absorption.

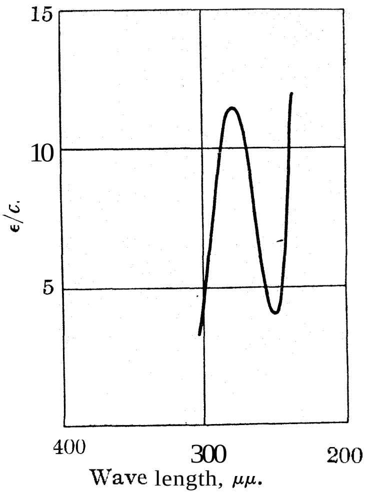

Fig. 1.

The light absorption of pseudoglobulin was measured both in electrolyte-free condition and in phosphate buffer at PH 5.5 (solution 0.019 *M* in KH_2PO_4 and 0.001 *M* in Na_2HPO_4). The position of the maximum was found to be 279 μμ and of the minimum 252 μμ. The extinction coefficient of the maximum was 11.5. In Fig. 1 the absorption curve is traced. The absorption of pseudoglobulin is markedly lower than the absorption of the original serum globulin.

Euglobulin was also examined with regard to light absorption. It was found to resemble very much the original serum globulin, being thus quite different from pseudoglobulin.

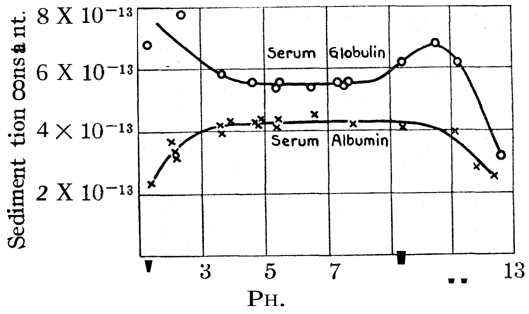

Fig. 2.

The PH-Stability Region of Serum Albumin and of Serum Globulin.—A number of sedimentation velocity runs were made in the oil-turbine ultracentrifuge[3] at 40,000–45,000 r. p. m. and 20° in the cell. The time of centrifuging varied from three to five hours. The solutions were brought to the desired concentration and PH immediately before starting the run.

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[2] T. Svedberg and B. Sjögren, THIS JOURNAL, 51, 3594 (1929).

[3] T. Svedberg, "Colloid Chemistry," 2d ed., Chemical Catalog Co , Inc., New York, 1928, p. 153.

TABLE III

SERUM ALBUMIN, SEDIMENTATION VELOCITY MEASUREMENTS

Solvent				PH of soln.	Concn. of protein, %	$s_{20°} \times 10^{13}$
Subs.	M	Subs.	M			
HCl	0.046	KCl	0.054	1.4	1.10	2.33
HCl	.007	KCl	.093	2.15	0.25	3.20
HCl	.007	KCl	.093	2.08	1.10	3.67
HCl	.007	KCl	.140	2.16	0.25	3.38
HAc	.018	NaAc	.002	3.60	1.10	3.98
HAc[a]	.018	NaAc	.002	3.64	0.25	4.16
HAc	.016	NaAc	.004	3.98	0.25	4.32
HAc	.008	NaAc	.012	4.8	0.25–1.25	4.21[b]
HAc	.008	NaAc	.012	4.8	0.25	4.34
HAc	.008	NaAc	.012	4.8	0.25	4.35
HAc	.008	NaAc	.012	4.8	0.71	4.40
HAc	.003	NaAc	.017	5.41	1.07	4.38
KH_2PO_4	.095	Na_2HPO_4	.005	5.46	0.18	4.12
KH_2PO_4	.050	Na_2HPO_4	.050	6.67	0.20	4.52
KH_2PO_4	.012	Na_2HPO_4	.188	7.82	1.10	4.21
NaOH[a]	.002	Na_2HPO_4	.032	9.40	1.10	4.01
NaOH[a]	.002	Na_2HPO_4	.032	9.40	1.10	4.05
NaOH[a]	.012	Na_2HPO_4	.026	11.10	0.70	3.99
NaOH[a]	.025	Na_2HPO_4	.017	11.80	0.55	2.84
NaOH	.050	NaCl	2%	12.40	0.55	2.54

[a] 1% in NaCl.

[b] Mean value of previous determinations.

TABLE IV

SERUM GLOBULIN, SEDIMENTATION VELOCITY MEASUREMENTS

Solvent						PH of soln.	Concn. of protein, %	$s_{20°} \times 10^{13}$
Subs.	M	Subs.	M	Subs.	M			
HCl	0.072	KCl	0.005	HAc	0.023	1.3	0.73	6.80
				NaAc	.023			
Same soln. after standing at 5° for 20 days								9.43
HCl	.025	KCl	.025	HAc	.023	2.46	0.75	7.93
NaOH	.023			NaAc	.023			
HAc	.180			NaAc	.020	3.67	0.75	5.94
HAc	.10			NaAc	.10	4.54	0.50	5.64
KH_2PO_4	.190			Na_2HPO_4	.009	5.5	0.12–1.00	5.66[a]
KH_2PO_4	.190			Na_2HPO_4	.009	5.41	1.08	5.37
KH_2PO_4	.140			Na_2HPO_4	.060	6.50	0.05	5.44
KH_2PO_4	.044			Na_2HPO_4	.156	7.27	.64	5.51
KH_2PO_4	.026			Na_2HPO_4	.174	7.57	.10	5.56
KH_2PO_4	.026			Na_2HPO_4	.174	7.57	.10	5.44
KH_2PO_4	.003	NaOH	.005	Na_2HPO_4	.031	9.41	.08	6.22
KH_2PO_4	.005	NaOH	.017	Na_2HPO_4	.026	10.56	.08	6.92
KH_2PO_4	.003	NaOH	.042	Na_2HPO_4	.017	11.22	.06	6.19
KH_2PO_4	.002	NaOH	.048	Na_2HPO_4	.003	12.52	.04	3.22
		NaCl	1%					
Same soln. after standing at 5° for 6 days								2.32
Same soln. after standing at 5° for 14 days								2.55

[a] Mean value of previous determinations.

The determinations of the sedimentation constant $s_{20°}$ are summarized in Tables 111 and IV and in the diagram, Fig. 2. For serum albumin the sedimentation remains constant from PH 4 to 9 and for serum globulin from 4 to 8. These PH ranges therefore represent the stability regions of serum albumin and serum globulin. The behavior of these proteins outside the stability regions will be discussed later.

The diffusion was found to be normal only in the vicinity of the isoelectric point. Both on the acid and the alkaline side of this point the diffusion was considerably depressed, indicating gel formation.[4]

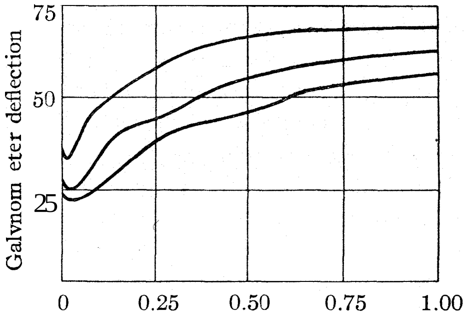

Fig. 3.

The Sedimentation of Pseudoglobulin and Euglobulin.—Two different preparations of pseudoglobulin were studied. The runs were made in the same way as in the case of serum albumin and serum globulin and at a *PH* of 5.5 (solutions 0.019 *M* in KH_2PO_4 and 0.001 M in Na_2HPO_4). The first material gave for the sedimentation constant $s_{20°} = 7.72 \times 10^{-13}$ in 0.13% solution, the second material $s_{20°} = 6.44 \times 10^{-13}$ in 0.10% solution and 6.52×10^{-13} in 0.60% solution. The diffusion constant showed considerable drift with time, indicating that the protein in question is a mixture of different molecules. The solutions also contained from 5–10% of non-centrifugible substance.

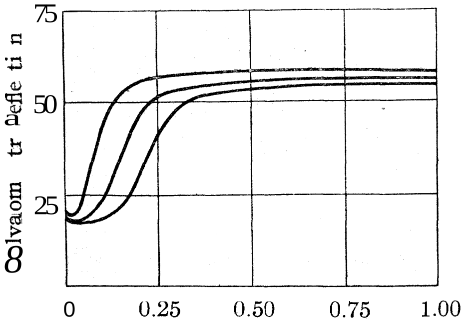

Fig. 4.

Euglobulin was centrifuged at a PH of 5.5 and in a phosphate buffer 0.190 *M* in KH_2PO_4 and 0.009 *M* in Na_2HPO_4. Two runs were made, one in 0.12%, the other in 0.63%, solution. Both runs gave sedimentation curves of a very peculiar shape, indicating that the protein material in question is a mixture of different kinds of molecules. In Fig. 3 the euglobulin sedimentation curves for the times thirty, fifty and seventy minutes after the start are given. For the sake of comparison Fig. 4 gives the corresponding serum globulin curves. In the case of serum globulin the shape of the curves is that of a simple molecular species, while the

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[4] Compare T. Svedberg and B. Sjögren, THIS JOURNAL, 51, 3594 (1929).

euglobulin curves show that this protein contains two different main constituents and probably some other component in lower concentration.

The splitting up of serum globulin into pseudoglobulin and euglobulin is not a reversible process. The sedimentation of a mixture of pseudoglobulin and euglobulin showed that the native serum globulin cannot be synthesized from these products by mixing them in the same proportion in which they are formed by dialysis of serum globulin.

The Molecular Weights of the Decomposition Products of Serum Albumin and of Serum Globulin.—The change in the value of the sedimentation constant at PH 4 and 9 in the case of serum albumin and PH 4 and 8 in the case of serum globulin indicates that at these hydrogen-ion concentrations the molecules of the serum proteins begin to disintegrate. Because of the anomalous diffusion it was not possible to calculate the molecular weights of the decomposition products from sedimentation velocity measurements. Earlier experiments have shown that sedimentation equilibrium determinations give the right value of molecular weight even in cases where the diffusion is depressed owing to gel formation or forces acting between the protein molecules. Sedimentation equilibrium runs were therefore made on serum albumin and serum globulin in the acid decomposition region. In the alkaline region the formation of non-centrifugible decomposition products renders such determinations uncertain.

Sedimentation equilibrium runs were further made on the isoelectric pseudoglobulin material studied above.

In Table V the equilibrium measurements are given.

TABLE V

DECOMPOSITION PRODUCTS OF SERUM ALBUMIN AND SERUM GLOBULIN. SUMMARY OF SEDIMENTATION EQUILIBRIUM MEASUREMENTS

Protein	Solvent		PH of soln.	Mol. wt.
Acid serum albumin	0 007 *M* in HCl	0 093 M in KCl	2 2	60,000 to 21,000
Acid serum albumin	007 M in HCl	.093 M in KCl	2 2	54,000 to 20,400
Acid serum globulin	025 M in HCl	025 M in KCl	2 5	59,000 to 23,000
	023 M in HAc	.023 M in NaAc		
	023 M in NaOH			
Isoelectric pseudoglobulin	019 M in KH_2PO_4 .001 M in Na_2HPO_4		5 5	99,300 to 53,200

The data of Table V confirm the conclusion drawn from the sedimentation velocity measurements. The acid serum albumin and serum globulin as well as the isoelectric pseudoglobulin are mixtures of molecules of different weight. Euglobulin was not studied in sedimentation equilibrium because the sedimentation velocity measurements had conclusively shown this protein to be a mixture of different molecular species.

The molecular weights of the acid serum albumin and serum globulin range from about 60,000 to about 20,000, those of the isoelectric pseudoglobulin from about 100,000 to about 50,000.

The Reversibility of the Acid and Alkaline **Decomposition.**—It is of considerable interest to state whether the decomposition of the serum albumin and serum globulin molecules in acid and alkaline solutions is reversible or not. In order to test the revcrsibility, solutions of serum albumin and serum globulin were brought to acid or alkaline reaction and left in this condition for a short time (from one hour to one day). The solutions were brought back into the stability region either by direct addition of the suitable reagents or by dialysis at low temperature against a buffer of the desired PH. Both procedures gave the same result. The sedimentation constant was found to have become normal again, which proves that the change is reversible. In Table VI the data are summarized.

TABLE VI

SERUM ALBUMIN AND SERUM GLOBULIN, REVERSIBILITY OF DECOMPOSITION

Subs., %	First solvent	Second solvent	PH of first soln.	PH of second soln.	$s_{20°} \times 10^{13}$ First soln.	Second soln.	Mean normal value
0.25 Serum albumin	0.007 *M* in HCl 0.093 *M* in KCl	0.008 *M* in HAc 0.012 *M* in NaAc	2.2	4.8	3.50	4.27	4.21
0.25 Serum albumin	0.007 *M* in HCl 0.093 *M* in KCl	0.008 *M* in HAc 0.012 *M* in NaAc	2.2	4.8	3.50	4.44	4.21
0.30 Serum albumin	0.017 *M* in Na_2HPO_4 0.025 *M* in NaOH	0.017 *M* in Na_2HPO_4 0.017 *M* in KH_2PO_4 0.025 *M* in NaCl	11.8	6.8	3.05	4.46	4.21
0.10 Serum globulin	0.017 *M* in Na_2HPO_4 0.025 *M* in NaOH	0.190 *M* in KH_2PO_4 0.009 *M* in Na_2HPO_4	11.8	5.5	5.05	5.77	5.66

Discussion of Results

The ultracentrifugal study of serum albumin and serum globulin at different hydrogen-ion concentrations has shown that the sedimentation constant is independent of PH within the range 4–9 for serum albumin and 4–8 for serum globulin. These PH ranges therefore represent the stability regions of these proteins. On the acid side of PH 4 and on the alkaline side of PH 9 the sedimentation of serum albumin decreases rapidly. Addition of potassium or sodium chloride does not effect any change in the sedimentation constant, showing that the Donnan potential is sufficiently eliminated. The diffusion is depressed, probably owing to gel formation, but there is not much drift in the diffusion constant with time. The material is therefore not very unhomogeneous. The sedimentation equilibrium runs in the acid region show that there are molecules of different weights present. The trend of the equilibrium curves (variation of molecular weight with distance from the center of rotation) indicates that the bulk of the material probably has a molecular weight between 30,000 and 40,000. It is therefore quite possible that the first stage in the acid (and alkaline) decomposition of serum albumin consists chiefly in disintegration into molecules of half the normal weight.

On the acid side of *PH* 4 the sedimentation constant of serum globulin increases with increasing acidity and also with time. The diffusion is depressed but also shows a considerable drift with time, indicating that the material is very unhomogeneous. The rapid sedimentation indicates aggregation of part of the decomposed protein. On the other hand, the sedimentation equilibrium run in the acid region shows that there is present a considerable amount of material with a molecular weight between 30,000 and 40,000. On the alkaline side of *PH* 8 the sedimentation at first increases with increasing alkalinity, reaches a maximum at a PH of about 10.5 and then decreases rapidly. The aggregation, therefore, is confined to a narrow *PH* region.

It is of interest to note that various investigators[5] have found that the salting out effect of, say, ammonium sulfate on the serum proteins is independent of PH from about 4 to about 9 and increases rapidly outside this acidity range. Thus Csapó and v. Klobusitzky[5c] found the salting out to be constant between *PH* 4.9 and 7.5 and a strong increase at 3.9 and at 9.3. Geill[5e] found constancy in the range 5.0–7.6 and a strong increase at 4.0. The region of constant salting out effect therefore corresponds fairly well with the PH stability region as determined by means of the ultracentrifugal analysis.

With regard to the nature of pseudoglobulin and euglobulin, the ultracentrifugal analysis has shown that both of these proteins are mixtures of molecules of different weight. The sedimentation constant of pseudoglobulin is considerably higher than that of native serum globulin. The diffusion constant shows a considerable drift with time, indicating that the material is very unhomogeneous. The equilibrium run gave values of molecular weight between 100,000 and 50,000. The heavier molecules which must be present to account for the high value of the sedimentation constant were probably too close to the bottom of the cell in the sedimentation equilibrium run to be noticed.

Euglobulin is still more unhomogeneous than pseudoglobulin. It is

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[5] (a) A. Homer, Biochem. *J.*, 11, 21 (1917); 13, 278 (1919); (b) St. Rusznyák, Biochem. *Z.*, 140, 179 (1923); *(c)* J. Csapó and D. v. Klobusitzky, ibid., 151, 90 (1924); (d) D. v. Klobusitzky, *ibid.*, 209, 304 (1929); *(e)* T. Geill, Dissertation, Kopenhagen, 1928.

characterized by the presence of very large particles settling rapidly during centrifuging. Tbe sedimentation curves (Fig. **3)** are of a peculiar shape, indicating the presence of two distinctly different groups of molecules. A mixture of pseudoglobulin and euglobulin is unhomogeneous with regard to sedimentation and is, therefore, not identical with the native serum globulin, which is quite homogeneous (Fig. 4). The opinion put forward by the present writers in the previous communication, *viz.*, that pseudoglobulin and euglobulin are but laboratory products which do not exist in the blood, is strongly supported by the above measurements.

The expenses connected with these experiments have been defrayed by a grant from the foundation "Therese och Johan Anderssons Minne."

Summary

1. The ultracentrifugal methods have been applied to the study of the PH stability region of serum albumin and serum globulin and to the study of the molecular weights of pseudoglobulin and euglobulin.

2. Serum albumin is stable within the PH range 4–9 and serum globulin within the range 4–8.

3. Outside the stability region the molecules of these proteins break up into smaller units. The first stage of the disintegration of the serum albumin molecule probably consists in the formation of molecules of half the normal weight. The breaking up of the serum globulin molecule is at first accompanied by the formation of aggregation products and then proceeds with the formation of products of lower molecular weight.

4. Pseudoglobulin and euglobulin are not homogeneous with regard to molecular weight, as is the case with both serum albumin and native serum globulin. Euglobulin is more unhomogeneous than pseudoglobulin and contains aggregates of large mass. It is not possible to regain the original serum globulin by mixing pseudoglobulin and euglobulin. The two latter proteins are to be regarded as laboratory products and are not present in the blood.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF BRISTOL]

THE REDUCTION OF QUERCETIN

BY T. MALKIN AND M. NIERENSTEIN

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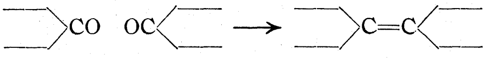
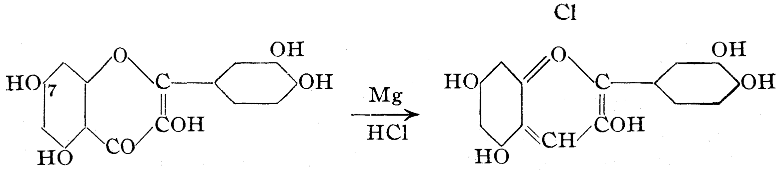
Whereas fluorone, xanthone, thioxanthone, acridone, anthraquinone and their derivatives yield dimolecular products on reduction in acid solution,[1]

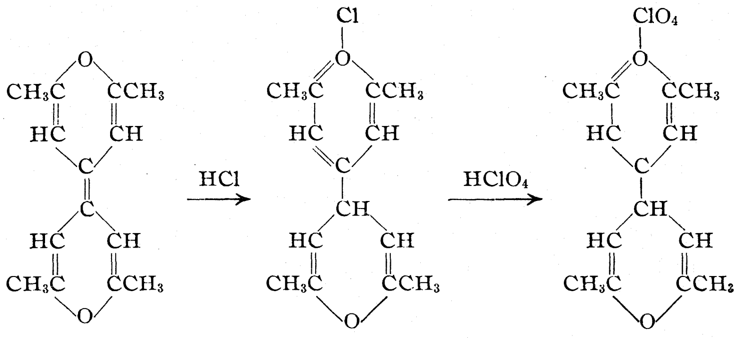


quercetin (I), under identical conditions, gives cyanidin chloride (II).[2]



I II

This is remarkable, considering that other pyrone derivatives behave normally, as shown by Baeyer and Piccard,[3] who found, for example, that dimethylpyrone, if reduced with zinc dust and hydrochloric acid, yields substance III, from which the crystalline perchlorate (IV) may be obtained.



III IV

This abnormal behavior of quercetin, as recorded by Willstatter and Mallison, and the importance of the production of cyanidin chloride from quercetin to the chemistry of the anthocyanidins, has led us to re-investigate this reaction.

The results obtained by us lead to the conclusion that quercetin behaves normally, giving the dimolecular product (V).

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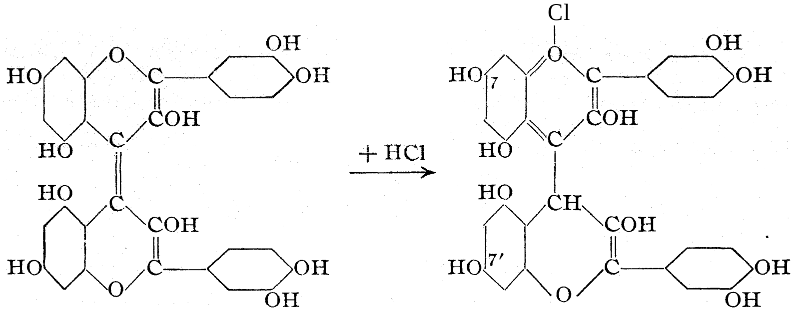
[1] See Houben, "Die Methoden der organischen Chemie," 3rd ed., Vol. II, 1925, pp. 270 ff.

[2] Willstatter and Mallison, *Sitzb. Preuss. Akad. Wiss.*, 769 (1914).

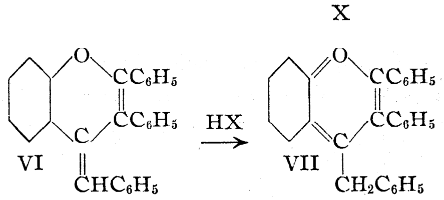
[3] Baeyer and Piccard, *Ann.*, 384, 208 (1911); 407, 346 (1914).



V

Following the nomenclature xanthylene (VIII), suggested by Kostanecki and Gurgenjanz[4] for the dimolecular reduction product from xanthone, the name *quercetylene chloride* is suggested for substance (V). The remarkable similarity between quercetylene chloride, $C_{30}H_{21}O_{12}Cl + 2H_2O$, and cyanidin chloride, $C_{15}H_{11}O_6Cl$, which not only resemble each other in almost all respects, but require exactly the same carbon content (C, 55.8), easily accounts for the fact that Willstatter and Mallison should have assumed that they had synthesized cyanidin chloride, since owing to the scarcity of material (0.165 g.) at their disposal, no chlorine analysis, which would have clearly emphasized the difference between these two substances, was possible.

The conversion of the intermediary reduction product, quercetylene, into quercetylene chloride (V), is in agreement with the observations of Baeyer and Piccard, already referred to, and also with the observations made by Lowenbein and Rosenbaum,[5] showing for example that a substance having structure (VI) is easily converted by acids into the pyryllium derivative (VII).



To test further our mechanism for the production of quercetylene chloride, we have also investigated xanthylene (VIII), from which we have obtained the ferrichloride (IX), and the diferrichloride (X), which were prepared according to the following scheme. The preparation of chlorides from xanthylene, however, presented some difficulties, which is to be expected in the light of Gomberg and Cone's[6] observation on the influence of hydroxyl groups on chloride formation.

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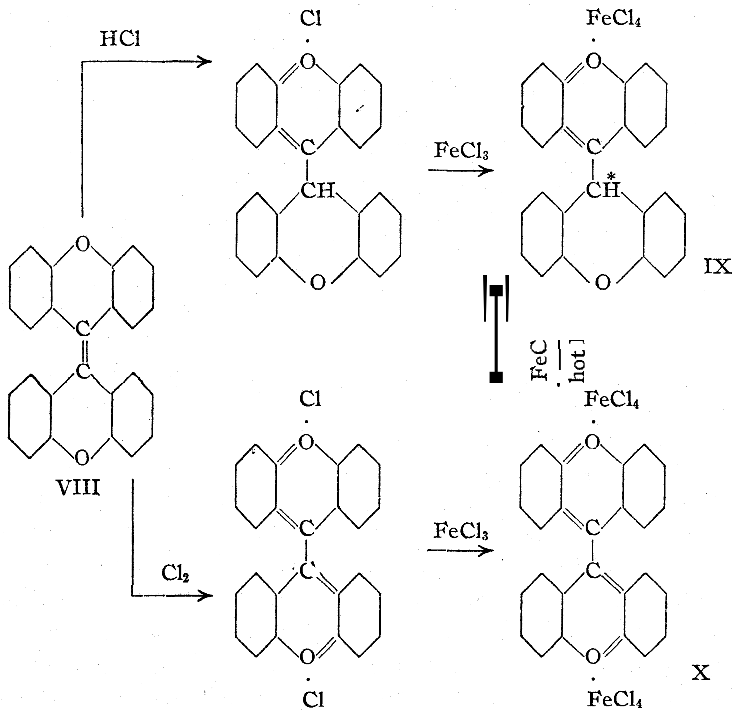
[4] Kostanecki and Gurgenjanz, *Ber.*, 28, 2310 (1895).

[5] Lowenbein and Rosenbaum, *Ann.*, 448, 233, 246 (1926).

[6] Gomberg and Cone, *ibid.*, **370,** 142–208 (1909).



The reduction of rhamnetin, 7, methylquercetin (compare I), which according to Robertson and Robinson[7] is reduced to rhamnetinidin chloride, 7-methylcyanidin chloride (compare II), also proceeds normally, leading to 7,7′-dimethylquercetylene chloride (compare VII). This product, freshly prepared, contains loosely bound hydrochloric acid, which it easily loses on standing, and then gives correct analytical values for 7,7′-dimethylquercetylene chloride. This loss of hydrochloric acid accounts for the unsatisfactory analytical data commented on by Robertson and Robinson,[8] who did not analyze for chlorine, and therefore assumed the increase in carbon content to be due to loss of water of crystallization.

Experimental

Quercetylene Chloride (V).—(1) The reduction product (0.2252 g.), prepared according to Willstatter and Mallison,[9] was purified by dissolving in 25 cc. of methyl alcohol, to which 25 cc. of 12% hydrochloric acid was added, the solution being concentrated on a water-bath. In this manner three fractions, resembling cyanidin chloride in their general properties, were obtained.

Anal. Subs. (dried in desiccator), 5.145, 4.555, 4.638 mg.: CO_2, 10.503, 9.284, 9.435 mg.: H_2O, 1.957, 1.577, 1.732 mg. Subs. (dried in desiccator), 3.70, 7.40, 5.507

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[7] Robertson and Robinson, J. *Chem. Soc.*, 2205 (1927).

[8] Ref. 7, p. 2206.

[9] Willstatter and Mallison, *Sitzb. Preuss. Akad. Wiss.*, 775 (1914).

mg.: AgCl, 0.879, 1.610, 1.196 mg. Subs. (dried by standing in high vacuum over NaOH for six days), 4.783 mg.: AgCl, 1.037 mg. Calcd. for $C_{30}H_{21}O_{12}Cl + 2H_2O$: C, 55.80; H, 3.91; Cl, 5.51. Found: C, 55.67, 55.58, 55.47; H, 4.23, 3.87, 4.15; Cl, 5.88, 5.38, 5.37, 5.36.

(2) To a boiling solution of 10 g. of quercetin in 300 cc. of acetic anhydride, 40 g. of zinc dust was added in three portions, causing the solution to turn deep red. After heating for forty-five minutes over a Bunsen flame, the cooled solution was poured into 500 cc. of 5% hydrochloric acid, the zinc dust being carefully extracted with hot glacial acetic acid. The light yellow colored reduction product was dissolved in 175 cc. of absolute alcohol and heated for two and one-half hours with 75 cc. of concentrated hydrochloric acid, during which time the solution turned deep red; 50 cc. of water was added, and the solution concentrated, a further 50 cc. of water being added after some time. The solid (8.5 g) which separated was collected, dried and then dissolved in 75 cc. of alcohol, to which was added 75 cc. of 12% hydrochloric acid. On concentration of the solution, 5.3 g. of prismatic crystals, containing only 3% of chlorine, was obtained. This product was rejected. On further concentration, 2.4 g. of a substance containing 5.5% of chlorine was obtained and dissolved in 50 cc. of methyl alcohol, the solution being concentrated in the presence of 50 cc. of 12% hydrochloric acid. Well-defined prisms which resembled the reduction product of Willstatter and Mallison in every respect were obtained.

Anal. Subs. (dried in desiccator), 9.108, 4.032 mg.: CO_2, 18.649, 8.237 mg.: H_2O, 3.361, 1.520 mg. Subs. (dried in desiccator), 5.132 mg.: AgCl, 1.098 mg. Calcd, for $C_{30}H_{21}O_{12}Cl + 2H_2O$: C, 55.80; H, 3.91; Cl, 5.51. Found: C, 55.85, 55.71; H. 4.11, 4.19; Cl, 5.29.

7,7′-Dimethylquercetylene Chloride (Compare V).—The reduction with zinc dust (40 g.) in acetic anhydride (100 cc.) was carried out according to Robertson and Robinson,[7] with the exception that not rhamnetin, but tetra-acetylrhamnetin (4.5 g.) was employed for the reaction. The use of acetylrhamnetin offered the advantage that instead of an ill-defined, sticky product, as observed by Robertson and Robinson, a definite yellow solid was obtained. The hydrolysis of this acetylated reduction product, as well as its purification, was carried out according to these workers, and the product obtained corresponded to theirs.

Anal. (Air-dried product) Subs., 3.191, 4.568 mg.: CO_2, 6.047, 8.657 mg.: H_2O, 1.304, 1.882 mg. Subs., 3.806 mg.: AgCl, 1.445 mg. Subs., 4.136 mg.: AgI, 2.608 mg. (Pregl–Zeisel). Calcd. for $C_{16}H_{13}O_6Cl + 2H_2O$ (rhamnetinidin chloride): C, 51.54; H, 4.56; Cl, 9.53; OCH_3, 8.32. Found: C, 51.68; 51.65; H, 4.57, 4.61; Cl, 9.39; OCH_3, 8.32. (Dried in desiccator.) Subs. (after standing for twenty-four hours). 5.219 mg.: AgCl, 1.558 mg. Found: Cl, 5.39. Subs. (after standing for four days), 5.613, 5.388 mg.: AgCl, 1.176, 1.101 mg. Found: Cl, 5.18, 5.06. Subs. (after standing for five days), 3.843 mg.: AgCl, 0.796 mg. Subs. (after standing for twelve days), 6.932 mg.: CO_2, 14.419 mg.: H_2O, 2.937 mg. Subs. (after standing for fifteen days), 8.332 mg.: CO_2, 17.362 mg.: H_2O, 3.520 mg. Calcd. for $C_{32}H_{25}O_{12}Cl + 2H_2O$: Cl, 5.25; C, 57.1; H, 4.34. Found: Cl, 5.12; C, 56.73, 56.84; H, 4.74, 4.73.

In connection with these analyses it is noteworthy that true pyryllium compounds have constant chlorine content; thus, for example, 3,5,7,3′,4′-pentahydroxyflavylium chloride, prepared according to Pratt and Robinson,[10] remains constant after standing in a desiccator for many months.

Anal. Subs., 5.494 mg.: AgCl, 2.301 mg. Calcd. for $C_{15}H_{11}O_6Cl + H_2O$: Cl, 10.42. Found: Cl, 10.36.

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[10] Pratt and Robinson, J. Chem. *Soc.*, 127, 172 (1925).

Xanthylene Ferrichlorides

Monoferrichloride (IX).—Into a suspension of 0.22 g. of xanthylene in 50 cc. of alcohol, gaseous hydrogen chloride was passed for fifteen hours at 0°. After standing overnight in the ice chest, the solution was filtered from the unchanged xanthylene (0.12 g.), and to the yellow solution a concentrated solution of ferric chloride in concentrated hydrochloric acid was added, until a cloudiness was produced, the solution being kept cool. The solution was diluted with concentrated hydrochloric acid, when, on standing, the ferrichloride separated in glittering, yellowish-brown scales which could not be recrystallized without decomposition, either from glacial acetic acid, benzene or alcohol. The product did not melt below 320°.

Anal. Subs., 4.549 mg.: CO_2, 9.199 mg.: H_2O, 1.317 mg. Subs., 6.650 mg.: AgCl, 6.879 mg. Calcd. for $C_{26}H_{17}O_2FeCl_4$: C, 55.81; H, 3.04; Cl, 25.40. Found: C, 55.15; H, 3.24; Cl, 25.66.

Diferrichloride (X).—To a suspension of 0.5 g. of xanthylene in 5 cc. of glacial acetic acid was added 5 cc. of glacial acetic acid saturated with chlorine. The reddish-brown solid formed was dissolved in 25 cc. of concentrated hydrochloric acid and to the red filtered solution was added a concentrated solution of ferric chloride in concentrated hydrochloric acid. The brick-red solid (0.4 g.) was crystallized from a large quantity of glacial acetic acid, brick-red, glittering prismatic needles which did not melt below 320°, being obtained.

Anal. Subs., 5.101, 4.388 mg.: CO_2, 7.802, 6.679 mg.: H_2O, 1.100, 0.895 mg. Subs., 8.085 mg.: AgCl, 12.236 mg. Calcd. for $C_{26}H_{16}O_2Fe_2Cl_8$: C, 41.27; H, 2.12; Cl, 37.57. Found: C, 41.71; 41.51; H, 2.41, 2.28; Cl, 37.44.

If, to a hot solution of 0.5 g. xauthylene in 250 cc. of glacial acetic acid, a concentrated solution of ferric chloride in concentrated hydrochloric acid was added, a deep red solution was produced instantaneously, deep red needles being deposited on standing. The product (0.7 g.) crystallized from a large quantity of glacial acetic acid in carmine-colored needles which did not melt at 320°. They proved to be a mixture of the mono- and diferrichlorides. This is in agreement with the results of Löwenbein,[11] who has shown that the hydrogen atom marked* in Formula (IX) is easily oxidized by ferric chloride in the pyryllium series. The production of a mixture consisting of (IX) and (X) is therefore evident.

Anal. Subs., 8.163, 5.244 mg.: CO_2, 13.098, 8.471 mg.: H_2O, 2.218, 1.403 mg. Subs., 3.528 mg.: AgCl, 4.867 mg. Calcd. for $C_{26}H_{17}O_2FeCl_4$; C, 55.81; H, 3.04; Cl, 25.40. Calcd. for $C_{26}H_{16}O_2Fe_2Cl_8$: C, 41.27; H, 2.12; Cl, 37.57. Found: C, 43.76, 44.06; H, 3.04, 2.99; Cl, 34.13.

In conclusion we wish to thank Miss C. M. Fear for all the analytical data recorded in this communication.

Summary

It is shown that the reduction of quercetin leads to a dimolecular reduction product, quercetylene chloride, instead of to cyanidin chloride, as stated in the literature; and that a similar reduction product, 7,7′-dimethylquercetylene chloride, is obtained from rhamnetin.

BRISTOL, ENGLAND

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[11] Lowenbein, *Ber.*, 57, 1517 (1924).

[Contribution from the Chemical Laboratory of the University of California]

THE INDUCED ADDITION OF ETHYLENE AND CHLORINE

By T. D. Stewart and Donald M. Smith[1]

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In a previous paper[1] it was shown that when chlorine gas and ethylene gas react at the surface of the containing vessel, there is formed momentarily a product which is not ordinary ethylene dichloride. This intermediate product may either react rapidly with chlorine to yield 1,1,2-trichloro-ethane and hydrogen chloride or it may be converted into stable ethylene dichloride. This latter step is promoted by oxygen. These changes are expressed in the following equations, the reactants being considered as gases although the reaction takes place upon the wall.

$$C_2H_{4(gas)} + Cl_{2(gas)} \xrightarrow{\text{catalyst}} C_2H_4Cl_2^* \qquad \text{(I)}$$

$$C_2H_4Cl_2^* \xrightarrow[\text{wall}]{O_2} C_2H_4Cl_{2(gas)} + 36{,}400 \text{ calories} \qquad \text{(II)}$$

$$C_2H_4Cl_2^* + Cl_{2(gas)} \longrightarrow C_2H_3Cl_3^* + HCl \xrightarrow{\text{Deactivator}} C_2H_3Cl_{3(gas)} + HCl_{(gas)} + 58{,}100 \text{ calories} \qquad \text{(III)}$$

The starred formula represents the intermediate compound of high energy content, which appears only at the surface and may involve the catalyst in its composition or be adsorbed upon the glass surface. Evidence that it is an activated form of ethylene dichloride is presented later.

We now propose to examine the mechanism by which the reaction energy is used to induce the first reaction (Equation I). This reaction is the rate determining step of the total reaction and its specific reaction rate is assumed to have two components. First there is the thermal component, or specific thermal reaction rate, with which the reaction energy is not concerned. This rate is determined by the catalytic conditions and the temperature. The reaction is autocatalytic under the conditions used and the catalyst is the reaction product, ethylene dichloride or trichloroethane, which, if present as a liquid film upon the surface, is considered to be of constant activity. The second component is the induced reaction rate, whose magnitude depends upon that of the thermal rate, and upon the length of the reaction chains[2]

$$C_2H_4 + Cl_2 \xrightarrow{\text{catalyst}} C_2H_4Cl_2^* \qquad \text{(I)}$$

$$C_2H_4Cl_2^* + C_2H_4 + Cl_2 \longrightarrow 2C_2H_4Cl_2^* \ldots\ldots \qquad \text{(Ia)}$$

and by Equation III

$$C_2H_3Cl_3^* + C_2H_4 + Cl_2 \longrightarrow C_2H_3Cl_3^* + C_2H_4Cl_2^* \ldots\ldots \qquad \text{(Ib)}$$

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[1] Stewart and Smith, This Journal, 51, 3082 (1929).

[2] The efficiency of propagation of the chains is very low, otherwise the reaction rate would approach that of an explosion. Occasional explosions in highly condensed systems support this mechanism.

If we assume that for the reaction product to act as a catalyst it must be activated, then for the thermal rate the activated catalyst is in thermal equilibrium with the main mass of the catalyst, whereas the induced component of the reaction is caused by the production during the reaction of activated catalyst in excess of thermal equilibrium.[3] The sum of these two components is the quantity experimentally determined and is termed the enhanced specific reaction rate.

The method of experimentation has already been described.

The Specific Thermal Reaction Rate

Subsequent to the series of experiments described in the previous paper, the addition reaction[4] was studied in the presence of oxygen to insure the minimum of any induced reactions. In this way the purely catalytic influence of trichloro-ethane and of ethylene dichloride could be compared.

Table I gives a summary of the results. In the last column the second order reaction rate constants are given as an arithmetical average of the various values calculated by intervals, together with the mean deviation

TABLE I

THE RELATIVE CATALYTIC EFFECTS OF LIQUID FILMS OF ETHYLENE DICHLORIDE, TRICHLORO-ETHANE AND OF A MIXTURE OF THE TWO, DEPOSITED UPON AN EVACUATED GLASS SURFACE, UPON THE RATE OF ADDITION OF ETHYLENE AND CHLORINE GASES

Pressures are in centimeters of mercury. $dx/dt = K''_a(a - x)(b - x)$. Pressure of oxygen, **35.0** cm.

Part **A.** Temperature, 20.0°

		Vapor pressure		Initial concentrations		K''_a X 10^3
Expt.	Catalyst	Initial	Final	Chlorine *(a)*	Ethylene (b)	(average)
7–2	$C_2H_4Cl_2$	**6.1**	**6.0**	**5.7**	**16.10**	1.8±0.10
7–3	$C_2H_3Cl_3$	**1.8**	**2 5**	**5.09**	**14 89**	1.3±0.15
7–4	Mixture	**3.6**	**3 9**	**4.28**	**15.59**	1.5±0.26
7–5	Mixture	**3.6**	**3.8**	**14 52**	**4.26**	1.3±0 **10**
7–6	Mixture	**3.6**	**4.5**	**13.51**	**13.43**	3.1±0.35
		Part B.	Temperature, 10.3°			
7–7	Mixture	**2.5**	**2.9**	**4.78**	**14.41**	3.7±0.15

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[3] Direct activation of ethylene and chlorine through collision, sufficient to bring about reaction, seems unlikely since alone they do not react at all upon dry glass surfaces. For the thermal reaction at least, the catalyst must be adsorbed upon the surface. The fact that the thermal reaction rate has a negative temperature coefficient indicates the reversible formation of a compound or "complex" between the catalysts and reactants.

[4] In this paper the term "addition reaction" refers to that series of steps as outlined above which results only in ethylene dichloride (I and II). The term "substitution reaction" correspondingly denotes trichloro-ethane as the sole (organic) product (I and III). The term "induced addition reaction" involves only the rate-determining step (Equation I, Ia or Ib) of these two reactions and indicates an enhanced rate of either addition or substitution, depending upon the nature of the following reaction. "Induced substitution" refers only to Equation III.

from the average. There was no pronounced trend in the constants for any one experiment.

The variation of the specific reaction rate with variation in the composition of the liquid phase is small, in the presence of a large amount of oxygen. The numerical magnitude of the constants reported in the previous paper are in good agreement when all the factors governing the reaction rate are considered. It would appear that ethylene dichloride is a better catalyst than is trichloro-ethane, but this conclusion is inconsistent with the data presented in the previous paper. It is believed that the trichloro-ethane is the better catalyst (when adsorbed) and is also a more efficient deactivator, so that the difference in reaction rates in Expts. 7–2 and 7–3 is simply an indication that the chain or induced part of the reaction is more inhibited by trichloro-ethane than by ethylene dichloride. As will appear later, chlorine is a powerful deactivator, so that its inability to reduce the constant in Expt. 7–5 to a lower value than 1.3×10^{-3} may be taken as an indication that this value, with the mixed liquids as catalyst, represents the true thermal specific reaction rate. It is important to note that large variations in the composition of the liquid film produce small changes (40%) in this specific reaction rate, as compared to the effect (1000%) of oxygen (see next section). In Table I we have the first indication of the effect upon the specific reaction rate of the *relative proportion* of the reactants. When either one is in excess, the reaction is slower, excess chlorine being more effective than excess ethylene in lowering the specific reaction rate. This fact alone indicates the existence of an induced addition reaction even in the presence of thirty-five centimeters' pressure of oxygen and with the mixed liquids as a film upon the surface. Excess of ethylene almost eliminates the chain reaction, and excess of chlorine reduces the reaction rate to the thermal value. Finally it must be presumed either that the catalytic activity of ethylene dichloride and of trichloro-ethane are nearly equal, or that only one (trichloro-ethane) is the effective catalyst, regardless of its relative amount. The latter view is supported by the existence of an inhibition period when saturated ethylene dichloride *vapor* is initially present but not in the presence of trichloro-ethane vapor. The catalyst is active only when adsorbed upon the wall, which accounts for the effectiveness of small amounts as compared to large amounts. On this view, liquid ethylene dichloride is not a strong catalyst, but as a liquid supports the induced part of the enhanced reaction rate.

The deactivating conditions described above seem adequate largely to eliminate the induced substitution (Equation III). For this purpose oxygen appears almost specific. Water vapor had little effect upon the substitution.

The Enhanced Reaction Rate

In the absence of oxygen the specific rate of the reaction is much greater than in its presence. Table II presents the results of some typical experiments.[5]

TABLE II

THE ENHANCED SPECIFIC REACTION RATE BETWEEN ETHYLENE AND CHLORINE IN THE ABSENCE OF OXYGEN, WATER OR LIGHT

Catalyst, liquid reaction products; temperature, 20.0°; pressures in cm. of mercury; time in minutes. A is the pressure of ethylene, B that of chlorine and x that of the ethylene used up, then, (1) $\frac{ds}{dt} = K_a''(A - x)(B - x)$ (2) $\frac{dx}{dt} = K_s''(A - x)(B - 2x)$. The constant is calculated by intervals, and the pressures correspond to the times of the first and last constant calculated.

	Expt. 5–9		Expt. 6 4		Expt. 6–5		Expt. 7–1	
	Partial pressures		Partial pressures		Partial pressures		Partial pressures	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
C_2H_4	11.72	7.15	14.25	0.64	15.93	13.02	15.30	13.01
Cl_2	7.35	0.35	27.5	1.25	6.02	0.10	5.2	0.22
Vapor	1.85	2.60	3.4	2.6	4.90	3.80	6.1	5.3
	Time	$K_s'' \times 10^3$	Time	$K_s'' \times 10^3$	Time	$K_s'' \times 10^3$	Time	$K_s'' \times 10^3$
	80	..	16	..	14	..	0	..
	81	8.7	17	11.5	15	11.1	1	10.6
	82	10.4	18	16.7	16	14.8	2	14.8
	83	13.7	19	18.2	17	15.5	3	28.1
	84	16.6	20	22.0	18	16.0	4	21.4
	85	$K_a'' \times 10^3$	21	34.6	19	14.7	5	13.8
	86	17.4	22	32.7	20	15.3	6	9.5
	87	17.9	23	32.7	21	11.9	7	7.1
	88	16.0	24	31.3	22	$K_a'' \times 10^3$	8	5.5
	89	16.0	25	31.3	25	10.8	9	6.5
	90	14.3	27	20.2	32	8.0		
	91	13.1	29	19.7				
	93	13.0	31	21.0				
	95	10.9	33	$K_a'' \times 10^3$				
	97	10.0	44	..				
	99	9.4	49	21.5				
	101	9.5	54	27.0				
	105	10.2	59	23.0				

The law for the reaction rate which is here used would not seem to be satisfactory, since a marked trend in the constants usually is found. Other laws, such as those involving other powers of the pressures than unity, were less satisfactory. Moreover, under deactivating conditions this law is very satisfactory and the increase in the magnitude of the constants over the values given in Table I, together with the trends, finds a reasonable explanation on the basis of the factors developed in the succeeding section.

The enhanced specific reaction rate is seen to be from five to twenty times that of the thermal rate. Accordingly, upon the assumption that the

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[5] If the reaction were mostly substitution, but partly addition, the addition reaction was presumed to occur exclusively at the end of the reaction when the chlorine concentration was low. There would be a short period in which the two reactions would be concurrent, *i. e.*, Equation I being succeeded in part by Equation II and in part by Equation III, but finally the latter would disappear.

thermal reaction initiates the induced chains, these chains are seen to involve on the average from five to twenty links. The product formed by the induced reaction is then over 80% of the total, and the enhanced rate is largely dependent upon factors affecting the induced reaction.

Discussion of Results

Variables Affecting the Enhanced Specific Reaction Rate.—These may be listed as follows: (1) catalyst for the thermal reaction, (2) the extent of the liquid film, **(3)** ratio of the pressures of the reactants, (4) actual pressures of the reactants, (5) deactivators other than the reactants and products, (6) temperature.

The first variable has already been considered. The other variables are used in tentative explanation of the apparent autocatalysis after separation of the liquid film, and the decrease in the constant toward the conclusion of the reaction (Table II).[6] Since the specific thermal reaction rate is constant in the presence of the liquid film and affected only slightly by small variations in its composition, this autocatalysis is to be ascribed to an effect upon the induced reaction of a changing condition within the film itself. The continued formation of the reaction products as liquids, with drainage to the bottom of the vessel, leads to a steady state condition of maximum opportunity for the induced reaction. The reaction within the liquid film (or accompanying its presence) is not thermally initiated, but is induced within the liquid phase by the thermal reaction occurring at the glass–liquid or glass–vapor interface. This statement is proved by the facts that separation of liquid in the presence of oxygen does not cause such a large increase in reaction rate, and that upon ordinary glassware the reaction is not autocatalytic. Hence the increasing reaction rate is connected with the setting up of a steady condition of the liquid film, modified by any changes in composition of the film during the reaction. A higher vapor pressure indicates a higher percentage of ethylene dichloride. This in turn permits an increased chance of induced addition reaction (greater specific enhanced reaction rate) and also an increased chance of the induced substitution reaction (Equation III). Thus in Expt. 7–1, in the presence of liquid ethylene dichloride and excess ethylene, the reaction is very rapid, somewhat autocatalytic (no inhibition period), and *completely substitution.*

The third and fourth variables account for the falling off in the specific reaction rate of the enhanced reaction. This phase of the work is still under investigation, since the evidence concerning them is confused with changing composition and character of the liquid film. Table I presents

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[6] At zero time there was no vapor present in Expt. 5–9 so that considerable time elapsed before the separation of liquid and any reasonable approach to constant catalytic conditions. In Expts. 6–4 and 6–5 there were 3.7 and 5.4 cm. pressure of ethylene dichloride present at zero time, respectively, and in Expt. 7–1 liquid ethylene dichloride was present at zero time.

the best evidence that the chance of an induced addition reaction is increased when the reactants are in equal concentrations. There is reason to believe the maximum chance should occur at this point under otherwise given conditions. Table III presents what other evidence there is that excess of either reactant in the absence of oxygen reduces the specific reaction rate.

TABLE III

THE EFFECT OF THE RELATIVE PROPORTIONS OF THE REACTANTS UPON THE SPECIFIC ENHANCED REACTION RATE UNDER FAIRLY CONSTANT CATALYTIC CONDITIONS AND UNIFORMITY OF LIQUID FILM

Temperature, 20.0°. All pressures are in cm. of mercury. No oxygen or water present.

Expt.	Vapor pressure	Pressure of reactants Chlorine	Ethylene	$K''_a \times 10^3$	$K''_s \times 10^3$
6 4	2.6	5.0	3.8	..	31
6-9	3.3	6.0	0.7		1.5
6 4	2.6	1.5	2.0	22	
5-9	2.1	1.5	8 5	16	
6-5	3 9	1.5	13.8		16
6-8	3.7	1.5	15.7	8	
7-1	5.8	1.5	13.6		25
6 4	2.6	7 5	5.0	32	
6-9	3.7	15.1	5.0		2.7
6 4	2.6	0.9	1.5	22	
6-9	3.3	7.7	1.5		2.5

Excess of chlorine is very effective in eliminating the chain reactions, excess of ethylene less so. The results of Expt. 7-1 again indicate that the composition of the liquid film is very important in determining the extent of the induced reaction, or the length of the reaction chains.

The chance that the reaction energy is used to induce further reaction is greatest when there is equal chance of collision of the reactants with the activating center. If there is a greater chance of chlorine molecules striking this center than of ethylene, the reaction energy will be dissipated among the chlorine molecules, and vice versa.[7] Thus a decrease in the specific rate constant is to be expected if one constituent is used up at a different

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[7] The inefficiency of propagation of the chains infers a high sensitivity to deactivators, which is inconsistent with the fact that the total quenching of the induced part of the reaction has been difficult to achieve. The answer to this anomaly may lie in part in the heterogeneous character of the reacting system; on the other hand, since both chlorine and ethylene may act as deactivators as well as reactants, the length of the chain may depend in part upon the ratio of their concentrations, and within limits be largely independent of their actual concentrations. This factor must be studied further, but it suggests that increase in reactant concentration automatically increases the deactivation capacity and, conversely, if one is depending upon excess of one reactant, as in the present instance, to help eliminate the chains, a very large excess may be required. Adsorbed oxygen, trichloro-ethane and chlorine appear to be the best deactivators, but none is effective in traces only.

rate than the other, leaving one in increasing excess as the reaction proceeds, and even at equal concentrations the specific reaction rate may decrease with decreasing concentration of the reactants. This was observable in Expt. 7–6 (Table I) in which, after the pressures of ethylene and chlorine fell to 2 cm. of mercury, the constant for the reaction dropped to the value 2.3×10^{-3}. A further explanation of this decrease in rate could be found in the idea that the uniformity of the film of liquid influenced the induced reaction. As the reaction slows, the rate of deposition of liquid lessens and the character of the film may change. The heterogeneous character of the reaction suggests other factors such as adsorption and diffusion which may play a smaller part in this effect.

The fifth and sixth variables require no further comment. Three experiments (not included above) made at 10.0° in the absence of oxygen indicate a negative temperature coefficient for the enhanced reaction rate, with some indication that at lower temperatures a positive coefficient might be found, *i. e.*, the induced reaction may disappear faster with lowering temperature than is compensated for by the negative temperature coefficient of the thermal reaction.

The Reaction Mechanism and the Nature of the Intermediate **Product.**—The equations presented above represent the proposed mechanism of the reaction. Only one mole of hydrogen chloride is formed for each mole of ethylene that reacts, even in the presence of liquid ethylene dichloride and excess of chlorine. It seems evident that the energy of addition is available to induce the exothermic substitution, and the substitution may induce the addition, but the total energy of the two reactions is not utilized to induce further chlorination. There are three possible reasons for this. First, the trichloro-ethane may rapidly distribute the excess energy to the walls, or other inert substances, before the collisions occur which are necessary to promote further substitution. Second, the energy may not be transferable from the trichloro-ethane to ethylene dichloride and chlorine in such a way as to induce substitution, even though collisions could take place during the life time of the energy laden trichloro-ethane. The total energy might be transferred to another molecule of the same kind, but not to one of a different kind. Third, the evolution of hydrogen chloride may be a factor in the rapid distribution of the reaction energy.

Whenever trichloro-ethane is formed, the chain reaction leading to *chlorination* is broken, and the question arises as to whether the reaction energy is ever actually transferred to a second molecule in such a way as to activate that molecule for a specific reaction. The induced substitution reaction (Equation III) need not presume such a transfer, since the molecule chlorinated may be the precise molecule formed in the addition reaction (Equation I). However, it was shown in the previous article that the presence of ethylene dichloride enhanced the chance of the substitution reaction, and that the presence of other substances, notably oxygen, decreased that chance.

This effect of the ethylene dichloride could be explained as follows. (1) Of all the deactivators present, ethylene dichloride is the only one which could receive the reaction energy and utilize it to promote a substitution. This presumes a transference of energy of high intensity from one molecule to another. The chance of an ethylene dichloride molecule possessing the energy would depend in part upon the relative concentrations of the various substances present and hence the chance of substitution would increase in the presence of ethylene dichloride. (2) Normal ethylene dichloride might prolong the life of an activated ethylene dichloride through association, or, in the liquid film, by offering mechanical protection or a medium of existence apart from the wall where it was formed. **(3)** Chlorine is a deactivator and, having received the energy of reaction, its chance of taking part in a substitution reaction would be enhanced by the presence of ethylene dichloride. However, the fact that when chlorine does act as a deactivator the amount of substitution does not exceed the maximum represented by the above equations, would appear to eliminate this view from serious consideration.

There is, then, good reason to believe that a normal ethylene dichloride molecule may receive the reaction energy, being itself activated sufficiently to react with chlorine; but the source of the energy is a "nascent" ethylene dichloride, termed above an "intermediate product," and except for their energy content the two molecules are identical. Equation II then becomes reversible under these specific conditions, *i. e.*, the source of the activation energy is an ethylene dichloride molecule of high energy content.

It should also be noted that although the reactions represented by Equations I and II may be reversible, the intermediate addition product is usually not in equilibrium with either the reactants or the final product during the reaction. Its formation is the slow step in the total reaction, and its rate of formation depends upon other processes, such as activations or complex formation, involving the reactants and catalysts. These in turn are in true equilibria, except as noted hereafter.

The thermal reaction requires a catalyst, which in the case of an evacuated glass surface is either ethylene dichloride or trichloro-ethane, or both, which are adsorbed.[8] The negative temperature coefficient of the rate of the reaction indicates an equilibrium involved in the rate determining step, of the type

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[8] If water is present it is preferentially adsorbed and the reaction is not autocatalytic. Upon a paraffin surface there is no adsorption and no reaction. It is probable that if the dry liquid reaction products were used as a solvent, in the dark, there would be little or no homogeneous reaction.

$$\text{Catalyst (activated or adsorbed)} + Cl_2 \rightleftarrows \text{Complex} + \text{Heat} \qquad \text{(IV)}$$

$$\text{Complex} + C_2H_4 \longrightarrow \text{Product (activated)} \qquad \text{(V)}$$

The equilibrium represented by Equation IV involves not the catalyst as a whole, but only that portion capable of entering into complex formation, such as some activated form. The reason that the surface-adsorbed catalyst is more effective than the liquid may be that adsorption stabilizes the complex formation or lowers the activation energy. To the extent that the catalyst may become activated in the liquid phase, a liquid phase reaction will take place.

It is then apparent that the intermediate reaction product (Equation I) is a potential catalyst itself, and represents an amount of activated catalyst in excess of that in true thermal equilibrium. By Equation IV this means a higher concentration of the complex chlorine addition product and hence a faster or enhanced specific reaction rate.

According to this picture of the mechanism, there is no essential difference between the thermal and the induced reactions. Photons, or any other source of activation within the liquid phase, might induce the reaction, and there is evidence[9] that light induces a gas phase reaction under the conditions of the present experiments. Of particular importance is the idea that by this mechanism the reaction energy need not be transferred at all from one molecule to another to induce the rate-determining step of the reaction. The presence of the liquid film brings about a faster reaction either by permitting the surface-formed intermediate to escape from the surface with its energy, thereby initiating a reaction chain within the liquid, or receives this energy by transfer with the same result.

Summary

The addition of ethylene and chlorine is probably a chain reaction, being self-induced. The role of the catalyst for the thermal reaction and the mechanism of the induced reaction are discussed.

BERKELEY, CALIFORNIA

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[9] To be presented in a separate communication.

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. VI. DERRIC ACID

BY F. B. LAFORGE AND L. E. SMITH

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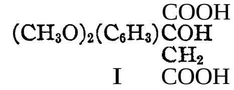
It has been established that the rotenone molecule is composed of two component parts which are joined together on the one hand by a chain of carbon atoms containing a carbonyl group and on the other by a lactone linkage.

Tubaic acid, $C_{12}H_{12}O_4$, corresponds to the first part and is obtained by boiling rotenone with alcoholic potassium hydroxide. Although a great deal has been learned about this cleavage product, its constitution has not yet been fully established, and it is at the present time the subject of further investigations.

Derric acid, which corresponds to the other half of the rotenone molecule, was isolated by us and described in a previous communication.[1] It is a dibasic acid having the formula $C_{12}H_{14}O_7$ and contains the original methoxyl groups of rotenone as well as the carboxyl group which, as the lactone group, is present in rotenone and many of its derivatives. Derric acid was prepared by peroxide oxidation of an acid having the formula $C_{23}H_{24}O_8$, which was obtained by treating dehydrorotenone with alcoholic potassium hydroxide, with or without the addition of zinc dust.[2] The yield of derric acid has been subsequently improved and it is now far more easily accessible than tubaic acid. Although its constitution is not yet fully established, we have nevertheless accumulated sufficient data to obtain a general idea of its nature. Derric acid is optically inactive. Oxidation by means of alkaline permanganate gives a dibasic acid which melts at 263° with evolution of carbon dioxide[3] and which is represented by the formula $C_{11}H_{12}O_7$. It forms a crystalline barium salt. Chromic acid oxidation of derric acid apparently gives the same compound but in much smaller yield. Energetic permanganate oxidation in neutral or acid solution destroys derric acid almost entirely, but in some experiments a very small yield of a monobasic acid was obtained which may have the formula $C_{10}H_{12}O_5$. However, the yield of this acid is at the best very small, and often none at all is obtained. In no case has it been possible to obtain a compound having the formula of a dimethoxybenzoic or dimethoxyphthalic acid.

All these facts indicate that derric acid is a dimethoxyphenylhydroxysuccinic acid of the formula and that its oxidation product is a dimethoxyphenyltartronic acid. Derric acid is thus the hydroxy



I

$$(CH_3O)_2(C_6H_3)\begin{array}{l}COOH\\COH\\CH_2\\COOH\end{array}$$

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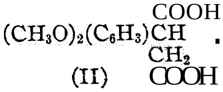
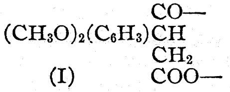
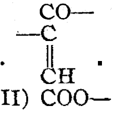
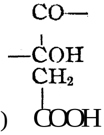
[1] LaForge and Smith, THIS JOURNAL, 52, 1091 (1930).

[2] Butenandt. *Ann.*, 464, 252 (1928).

[3] Derric acid itself does not evolve gas on fusion.

derivative of the acid which corresponds to the second part of the rotenone molecule and which would itself be a dimethoxy-phenylsuccinic acid of formula  $\begin{array}{l} \qquad\qquad\quad COOH \\ (CH_3O)_2(C_6H_3)CH \\ \qquad\qquad\quad CH_2 \\ \qquad\qquad\quad COOH \end{array}$ (II). We are now attempting the synthesis of these acids.

Butenandt, in his most recent article,[4] gives considerable attention to dehydrorotenone and other compounds of the dehydro series. He advances the suggestion that the loss of the two hydrogen atoms involved in the formation of the dehydro compounds takes place in the half of the molecule which we represent by derric acid and not in that half corresponding to tubaic acid. This is a possibility which we have also considered. In many respects such a theory is in close agreement with the facts. For instance, if the grouping involved is represented by the partial formula I,  $\begin{array}{l} \qquad\qquad\quad CO- \\ (CH_3O)_2(C_6H_3)CH \\ \qquad\qquad\quad CH_2 \\ \qquad\qquad\quad COO- \end{array}$ (I), then the formation of dehydrorotenone could be represented by the change to III.  $\begin{array}{l} \quad CO- \\ -C \\ \quad \| \\ \quad CH \\ \quad COO- \end{array}$ (III). Also, dehydrodihydroxyrotenonic acid $C_{23}H_{24}O_8$ (derris saure according to Butenandt) might contain the grouping IV  $\begin{array}{l} \quad CO- \\ \quad | \\ -COH \\ \quad CH_2 \\ \quad | \\ \quad COOH \end{array}$ (IV) which in turn would be expected to yield derric acid on oxidation. Furthermore, tubaic acid does not yield dehydrotubaic acid.

We have, however, abandoned this theory for the following reasons. First, dehydrorotenone and its analogs dihydrodehydrorotenone and dehydroisorotenone are formed by dehydration of hydroxyl derivatives.' As far as this goes, it is also possible that these hydroxy derivatives could contain the grouping IV but with the lactone group still intact, and that the elements of water could be extracted to form dehydrorotenone and then two molecules of water added again to form the acid of formula $C_{23}H_{24}O_8$, with the opening of the lactone ring. In that case the hydroxyl derivatives (rotenolone, etc.) would be expected to give the same acid as the corresponding dehydro derivatives. Nothing of the kind happens, but rotenolone or acetylrotenolone on treatment with zinc and alcoholic potassium hydroxide yield rotenol and derritol exactly as does rotenone itself. Moreover, if the acid $C_{23}H_{24}O_8$ did actually contain the grouping IV, then it should be easily dehydrated by alcoholic sulfuric acid; but instead of such a reaction taking place, simple esterification results and a quantitative yield of the ethyl ester of the original acid is obtained.

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[4] **Butenandt, *Ann.*, *477*, 245 (1930).**

Second, although formula III contains an acid methylene group which might react with oxidizing reagents to form diketones of the rotenonone type, we have shown that such derivatives are in all cases derivatives of the dehydro series[1] which would not contain the necessary methylene group according to the above scheme.

Third, it is difficult to understand how the loss of two hydrogen atoms in the part of the molecule represented by derric acid could so alter the properties of the whole molecule with respect to the formation of derritol.

Although we realize that the scheme which we have already proposed[5] to explain the dehydro derivatives is open to objections, we have nevertheless preferred it to the theory which we have discussed above.

Derric Acid.—Two grams of dehydrodihydroxyrotenonic acid of formula $C_{23}H_{24}O_8$ is dissolved in 25 cc. of 5% potassium hydroxide. The solution is warmed to 60°, and 6 cc. of 30% hydrogen peroxide added in small portions, after which it is boiled to remove any excess hydrogen peroxide. The reaction is complete when a test portion of the solution, diluted with water, gives no precipitate on acidifying with hydrochloric acid. Usually there is formed a small amount of a black precipitate which is removed mechanically. A slight excess of hydrochloric acid is added, and the solution is extracted with ether. The ether solution is dried with sodium sulfate and the solvent removed. The resulting crystalline material is washed with chloroform and recrystallized by dissolving in ethyl acetate and adding warm n-butyl ether. The compound melts at 171°. The yield varies somewhat but averages 0.45 g. of recrystallized acid.

Subs., 0.1806 g. in 10 cc. of water showed no rotation in a 1-dm. tube, $[\alpha]_D$ 0.

Oxidation of Derric Acid.—Eight-tenths of a gram of derric acid is dissolved in 100 cc. of water, and the solution is made slightly alkaline with potassium hydroxide. The solution is heated on the steam-bath, and 1.8 g. of potassium permanganate dissolved in 100 cc. of water is added in small portions. After the manganese dioxide has settled out the solution is filtered and the filtrste evaporated to a small volume. When the solution is acidified with hydrochloric acid, a white crystalline precipitate is formed which is filtered off and recrystallized from water. The substance crystallizes in two forms, one of which contains water of crystallization. When dried at 110° it melts at 261–263°. The yield is 0.5 g.

Anal. Subs., 0.0646, 0.0645: CO_2, 0.1220, 0.1221; H_2O, 0.0270, 0.0263. Calcd. for $C_{11}H_{12}O_7$: C, 51.56; H, 4.68. Found: C, 51.50, 51.66; H, 4.65, 4.53. Subs., 0.0207: cc. of $N/10$ KOH, 1.55. Calcd. mol. wt.: 256. Found: 266.

Barium Salt.—One gram of the acid was dissolved in 20 cc. of hot water, and a hot solution of barium hydroxide was added until the solution was slightly alkaline. The barium salt crystallized out at once and was dried at 110°.

Anal. Subs., 0.1505: $BaSO_4$, 0.0890. Calcd. for $C_{11}H_{12}O_7$: Ba, 35.05. Found: 34.8.

The original acid was obtained when the barium salt was dissolved in water and the barium removed with sulfuric acid; melting point, 263°.

Anal. Subs., 0.0636: CO_2, 0.1210; H_2O, 0.0263. Calcd. for $C_{11}H_{12}O_7$: C, 51.66; H, 4.68. Found: C, 51.87; H, 4.59.

When 0.8 g. of derric acid in 100 cc. of water with the addition of 1 g. of magnesium sulfate was oxidized by adding 1 8 g. of potassium permanganate in 100 cc. of water in the same manner as described above, another acid was sometimes obtained with a

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[5] LaForge, THIS JOURNAL, 52, 1102 (1930).

maximum yield of 0.07 g. It melted at 183° and was probably a monobasic hydroxy acid. This acid has not been available in sufficient quantity for satisfactory study.

Anal. Subs., **0.0520, 0.0520:** CO_2, **0.1095, 0.1098;** I-120, **0.0272, 0.0266.** Calcd. for $C_{10}H_{12}O_5$: **C, 56.6;** H, **5.66.** Pound: **C, 57.41, 57.57;** H, **5.81, 5.68.** ***Titration.*** Subs., **0.0159: 0.7** cc. of *N*/10 KOH. Calcd. mol. wt.: **212.** Found: **227.**

Dehydrodihydroxyrotenonic Acid Ethyl Ester.—One gram of the acid was boiled for three hours in **10** cc. of 10% alcoholic sulfuric acid. The ester crystallized on cooling and was recrystallized from 95% alcohol. It crystallized in needles melting at 98°. The yield was nearly quantitative.

Anal. Subs., **0.0704:** CO_2, **0.1092;** H_2O, **0.0383.** Calcd. for $C_{25}H_{28}O_8$: **C, 65.78;** H, 6.14. Found: C, 65.55; H, 6.04.

Summary

Derric acid of formula $C_{12}H_{14}O_7$ which is obtained by peroxide oxidation of dehydrodihydroxyrotenonic acid of formula $C_{23}H_{24}O_8$ is oxidized by permanganate to a new dibasic acid of formula $C_{11}H_{12}O_7$ having the properties of a dimethoxytartronic acid. It seems likely that the rotenone molecule contains the grouping corresponding to a dimethoxyphenylsuccinic acid. Such an assumption might explain the formation and properties of dehydrorotenone. A possible explanation of the formation of dehydrodihydroxyrotenonic acid by the addition of the elements of water to the double bond is open to theoretical objections.

WASHINGTON, D. C.

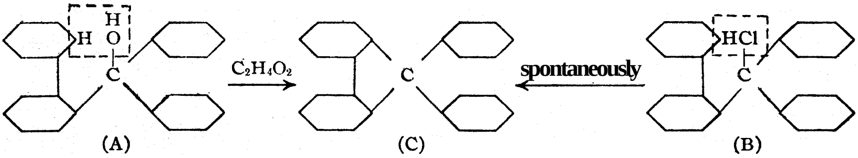
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

SPIRANS WITH FOUR AROMATIC RADICALS ON THE SPIRO CARBON ATOM[1]

BY R. G. CLARKSON AND M. GOMBERG

RECEIVED FEBRUARY 24, 1930 PUBLISHED JULY 3, 1930

Ullmann and Wurstemberger,[2] by heating the crude 2-phenyltriphenylcarbinol (A) with sulfuric acid, and Khotinsky and Patzewitch[3] by heating the same with acetic acid obtained 9,9-diphenylfluorene (C). We have now succeeded in preparing the carbinol pure and in crystalline state, but our attempts to convert it into carbinol chloride (B) resulted invariably



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[1] Part of a dissertation submitted by R. G. Clarkson to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Science, **1929.**

[2] Ullmann and Wurstemberger, ***Ber., 38,*** **4105 (1906).**

[3] Khotinsky and Patzewitch, *ibid.*, 42, **3106 (1909).**

in the formation of the same diphenylfluorene, ever, when the mildest conditions of procedure were employed.

We then prepared 9-(2-biphenyl)-9-fluorenol, anticipating greater stability both for this carbinol and its carbinol chloride. The fluorenol could indeed be recrystallized unchanged from acetic acid, but the addition of a drop of hydrochloric acid to the solution brought about an immediate closure of the ring. The compound so formed, *spiro*-bifluorene (Formula I, Table I), is the simplest possible representative of that class of spirans in which the spiro carbon atom is linked by all its four valencies to groups of the purely aromatic series. Very few examples of such spirans are described in the literature.[4] This proneness of the o-biphenyl and other similar groups toward ring closure we have now sought to utilize in extending our knowledge of the new type of spirans. A list of those which have been prepared is given in Table I, indicating the carbinols that give rise to the spirans. The names of the carbinols and the corresponding spirans are given in the experimental part.

Experimental

2-Phenyltriphenyl Carbinol.—2-Aminobiphenyl[5] was converted into 2-cyanobiphenyl by essentially the same procedure as has been since described by Schlcnk and Bergmann;[6] b. p. 202–204° at 43 mm. As these authors give for their substance a melting point of 41°, and ours, after recrystallization, melted at 35–36", we have further verified the constitution of the compound by synthesizing it from o-cyanodiazonium hydroxide and benzene.[7]

2-Phenylbenzophenone was obtained by the action of phenylmagnesium bromide upon 2-cyanobiphenyl with a yield of 76%. When reduced with magnesium–magnesium iodide mixture,[8] the ketone gives, instead of the expected pinacol, 9-phenylfluorene, but only in 25% yield.

A solution of 6.5 g. of 2-phenylbenzophenone in 50 cc. of ether was added to a solution of phenylmagnesium bromide obtained from 8 g. of bromobenzene. After refluxing overnight, the solid magnesium carbinol salt was filtered off and decomposed with an ice-cold solution of ammonium chloride. The crude solid carbinol was filtered from the aqueous solution of the salts, dried and recrystallized from a mixture of benzene and petroleum ether as large, slightly yellow clumps; m. p. 87–88'; yield, 5.2 g., or 63%.

Anal. Calcd. for $C_{25}H_{20}O$: C, 89.25; H, 6.00. Found: C, 89.05; H, 5.85. Mol. wt. (in benzene). Calcd.: 336. Found: 338.

The failure of previous investigators[2,3] to obtain this carbinol in the solid state may be attributed to the partial decomposition of the carbinol in their process of steam distillation. The substance can be safely steam distilled only if every trace of acid is previously removed.

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[4] Radulescu, in the "Publications de l'Institut Chimique de Cluj," 1926–1928, Vols. I–V, supplies a fairly complete bibliography on spirans. We desire to express to Dr. Radulescu our appreciation for a copy of these publications.

[5] Graebe and Rateanu, *Ann.*, 279, 257 (1894).

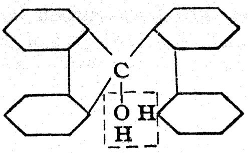
[6] Schlenk and Bergmann, *ibid*, 464, 33 (1928).

[7] Gomberg and Bachmann, THIS JOURNAL, 46, 2339 (1924).

[8] Gomberg and Bachmann, *ibid.*, 49, 236 (1927).

TABLE I

FORMULAS OF COMPOUNDS



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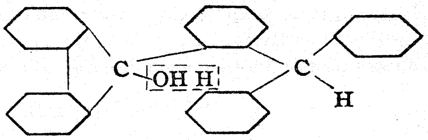

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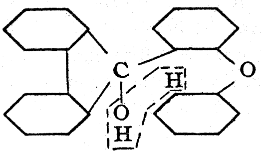

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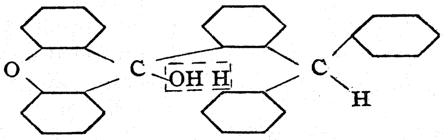

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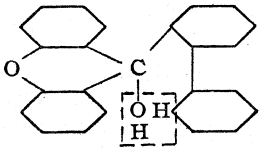

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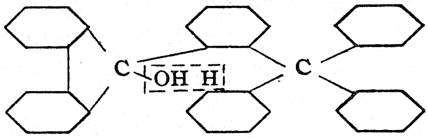

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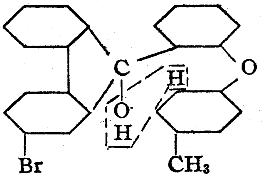

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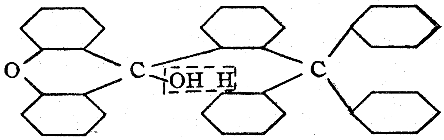

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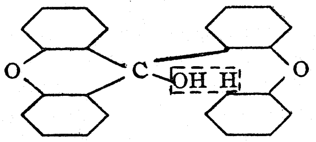

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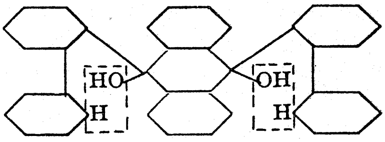

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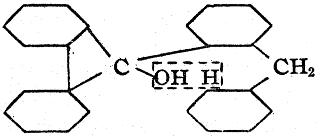

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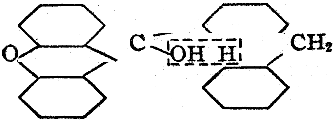

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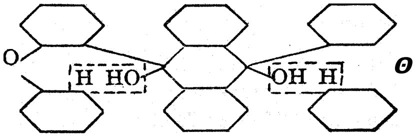
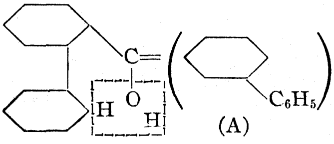


O XII

When a solution of the carbinol in acetic acid is heated, an orange-red color develops: after a few minutes of boiling the liquid becomes filled with crystals of the colorless diphenylfluorene (Formula C) and the color of the solution fades completely.

All attempts to prepare the carbinol chloride yielded the same hydrocarbon (C). The chloride evidently passes over into the fluorene spontaneously, for treatment of the carbinol with acetyl chloride, even at 0°, produces the fluorene.

9,9-Di-(3-biphenyl)-fluorene



(A)

An analog of 2-phenyltriphenyl carbinol, namely, 2,3′,3″-triphenyltriphenyl carbinol, was prepared from 3-bromobiphenyl and the ester of 2-phenylbenzoic acid. The crude carbinol resisted all efforts to obtain it crystalline. It was converted into 9,9-di-(3-biphenyl)-fluorene (A) by heating an acetic acid solution of the carbinol with a few drops of sulfuric acid and formed colorless crystals; m. p. 190–193°.

Anal. Calcd. for $C_{37}H_{26}$: C, 94.43; H, 5.57. Found: C, 94.09; H, 5.48. Mol. wt. (in benzene). Calcd.: 470. Found: 480.

9,9′-Spirobifluorene (I)

9-(2-Biphenyl)-9-fluorenol.—2-Iodobiphenyl was prepared from the amino compound by Sandmeyer's reaction, b. p. 183–186" at 32 mm. Our yield was usually 75%, and the iodide reacted directly with ordinary magnesium, requiring no agency for activation.[9] To the Grignard reagent from 14.0 g. of 2-iodobiphenyl was added 9 g. of fluorenone in small portions; the mixture was refluxed overnight on a steam-bath. The yellow precipitate was filtered, washed with a little absolute ether and decomposed with ice and ammonium chloride. The carbinol was filtered, dried and recrystallized from alcohol, or from a mixture of benzene and petroleum ether as colorless prisms; m. p. 169–170°; yield, 70%.

The compound is more stable than 2-phenyltriphenyl carbinol; a pure sample may be recrystallized unchanged from glacial acetic acid. The crude carbinol, which contains traces of adsorbed iodine, is converted to the spiran by such treatment.[10]

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.78; H, 5.43. Found: C, 90.05; H, 5.27. Mol. wt. (in benzene). Calcd.: 334. Found: 330.

The Spiran (I).—One drop of hydrochloric acid was added to a boiling solution of 5.0 g. of the above fluorenol in 10 cc. of acetic acid. Boiling was continued for a minute or two until the yellow color disappeared, and water was then added to the hot solution until the latter became turbid. After cooling the solution, the large glistening plates of spiran were filtered and dried. A further quantity of the product was obtained by diluting the filtrate with water. The compound may be recrystallized from alcohol or from a benzene–petroleum ether mixture; m. p. 198–199°; yield, 4.0 g.

The spiran was also obtained by allowing a benzene-acetyl chloride solution of the carbinol to stand overnight at room temperature. Evaporation of the solvent yielded large prisms of the hydrocarbon. The substance is not affected by boiling with zinc dust and acetic acid, and does not add bromine.

Anal. Calcd. for $C_{25}H_{16}$: C, 94.90; H, 5.10. Found: C, 95.07; H, 5.11. Mol. wt. (in benzene). Calcd.: 316. Found: 316.

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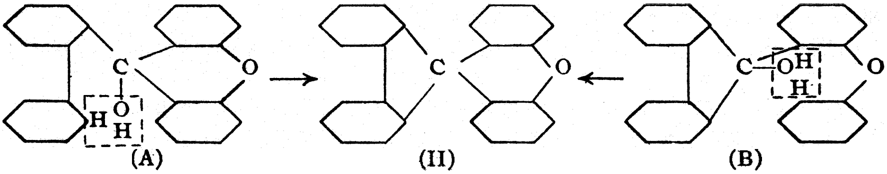
[9] Gilman, Kirhy and Kinney, This Journal, 51, 2261 (1929), gave a yield of 51.7%, and used activated copper-magnesium alloy to start the Grignard reaction.

[10] Compare Ref. 8, p. 246,

Spiro-9-fluorene-9'-xanthene (II)

A definite proof concerning the course of our condensation reaction would be afforded if the same spiran (II) resulted (1) on the one hand from 9-(2-phenoxyphenyl)-9-fluorenol (A), and (2) on the other hand from 9-(2-biphenyl)-9-xanthenol (B). Such is the case.



(1) Synthesis of the Spiran (II) from 9-Flurenone

2-Iododiphenyl Ether.—The method of Jones and Cook[11] was used in preparing 2-nitrodiphenyl ether, except that o-chloronitrobenzene was substituted for the o-bromo compound and the reaction was carried out at 150 instead of 100". The nitro ether was reduced to the amino ether, and through Sandmeyer's reaction converted into the iododiphenyl ether.

The iodide boils at 198–202° at 32 mm.; m. p. 54–56°.

Anal. Calcd. for $C_{13}H_9OI$: I, 42.72. Found: I, 42.88. Mol. wt. (in benzene). Calcd.: 296. Found: 289.

9-(2-Phenoxyphenyl)-9-fluorenol (Formula A).—It is necessary to use a large volume of ether in preparing the Grignard reagent from the above iodide since the halo-magnesium compound is likely to crystallize from concentrated solutions upon the metal in large compact prisms. After boiling a solution of 8.9 g. of the 2-iodo compound in ether for two hours with 0.73 g. of magnesium, the metal had completely dissolved. A solution of 5.4 g. of fluorenone was added and the mixture was refluxed overnight. The insoluble magnesium product was filtered, washed with a little ether, and decomposed with ice and ammonium chloride. The recrystallized carbinol, slightly brown clumps, melted at 154°; yield, 5.7 g.

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.68; H, 5.18. Found: C, 85.47; H, 5.02. Mol. wt. (in benzene). Calcd.: 350. Found: 354

The Spiran (XI).—Three g. of the carbinol was boiled for a few minutes with a mixture of 10 cc. of acetic acid and 3 cc. of acetyl chloride. Upon cooling the solution, glistening colorless crystals of spiran were obtained; m. p. 212–213"; yield, 2.2 g.

Anal. Calcd. for $C_{25}H_{16}O$: C, 90.33; H, 4.85. Found: C, 90.28; H, 4.70. Mol. wt. (in benzene). Calcd.: 332. Found: 325.

This spiran is the mother substance of the dihydroxycarboxylic acid described by Bischoff and Adkins.[12]

(2) Synthesis of the Spiran (II) from Xanthone

A solution of 4.9 g. of xanthone in 60 cc. of hot benzene was added to the Grignard reagent from 7 g. of 2-iodobiphenyl and the reaction mixture boiled overnight. The insoluble magnesium salt was separated and decomposed in the usual way, and the crude product purified. The pure material crystallized in colorless needles from a mixture of benzene and petroleum ether; m. p. 130°; yield, 4.3 g.

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[11] Jones and Cook, This Journal, 38, 1537 (1916).

[12] Bischoff and Adkins, *ibid.*, 45, 1030 (1923).

Analysis indicated that the substance was not the expected xanthenol (B), but a molecular compound of (B) with xanthone in the ratio of one to one. Similar compounds have been reported by others.[13] In solution, dissociation into the components ensues, as is shown by the molecular weight determination made upon the complex. The free carbinol (B) could not be obtained directly from the double compound; but after conversion of the xanthenol component of the complex to the spiran (11), the xanthone, which remained unchanged, could be readily removed.

Anal. Calcd. for ($C_{25}H_{18}O_2 + C_{13}H_8O_2$): C, 83.29; H, 4.80. Found: C, 83.49; H, 4.82. Mol. wt. (in benzene). Calcd. for (350 + 196) ÷ 2 = 273. Found: 275.

One gram of the double compound was dissolved in 20 cc. of acetic acid and warmed on the steam-bath for three hours. Crystals of the spiran slowly separated, 0.52 g. being obtained. From the mother liquor 0.22 g. of pure xanthone was isolated. The spiro compound obtained in this way melted at 212". Mixed with the spiran prepared from the fluorenol **(A)** it melted at 212–213°. The structure of the spiran is thus definitely established since it must contain both the fluorene and xanthene rings.

Spiro-9-(2-bromofluorene)-9′-(2′-methylxanthene) (III)

2-Iodo-4'-methyl-diphenyl Ether.—2-Nitro-4'-methyl-diphenyl ether was prepared[14] by a procedure similar to that for 2-nitrodiphenyl ether, from potassium *p*-cresylate and o-chloronitrobenzene. The amine was obtained from the nitro compound and was then converted into the iodide. The iodide distilled at 210–215° at 34 mm. and solidified to a mass of colorless needles; m. p. 41°; yield, 74%.

Anal. Calcd. for $C_{13}H_{11}OI$: I, 40.72. Found: I, 40.94. Mol. wt. (in benzene). Calcd.: 310. Found: 313.

9-(2-Phenyl p-Tolyl Ether)-6-bromo-9-fluorenol.—The direct bromination of fluorene[15] was used to prepare 2-bromofluorene. The employment of repeated crystallizations suggested by these authors was avoided by distilling the crude product under reduced pressure; b. p. 234–239° *at* 48 mm.; m. p. 110°; yield, 65%. The bromofluorene was oxidized with sodium dichromate and acetic acid, and the fluorenone twice recrystallized from glacial acetic acid as beautiful yellow needles; m. p. 143–145°.[16]

A solution of 15.5 g. of 2-iodo-4'-methyl-diphenyl ether in absolute ethyl ether was boiled with 1.2 g. of magnesium for four hours on a steam-bath. One hundred cc. of benzene was then added and 12.9 g. of 2-bromofluorenone was introduced in small portions. The mixture was refluxed overnight and the insoluble product was then filtered and decomposed in the usual way; yield, 14 g. The pure carbinol formed pale yellow cubical crystals and melts at 175°.

Anal. Calcd. for $C_{25}H_{19}O_2Br$: Br, 18.03. Found: Br, 18.04. Mol. wt. (in benzene). Calcd.: 443. Found: 441.

The Spiran **(III)**.—Heating a concentrated solution of the above carbinol in glacial acetic acid, to which a few drops of concentrated hydrochloric acid had been added, produced the spiran as colorless needles; m. p. 201°.

Anal. Calcd. for $C_{26}H_{17}OBr$: Br, 18.90. Found: Br, 18.63. Mol. wt. (in benzene). Calcd.: 425. Found: 427.

We had hoped to convert the methyl group to a carboxyl group, which would enable us to form salts of the spiran with optically active bases, and thus perhaps re-

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[13] Schlenk and Hertzenstein, ***Ann.***, **372,** 27 (1910); Ref. 8, p. 253.

[14] Cook and Sherwood, THIS JOURNAL, **37,** 1835 (1915).

[15] Courtot and Vignati, Bull. *soc. chim.*, [4] 41, 58 (1927).

[16] Gomberg and Pernert, THIS JOURNAL, 48, 1378 (1926), give 149°.

solve the acid into its stereoisomers. The effort was unsuccessful, since the methyl group could not be oxidized without destroying the spiran linkage.

9,9′-Spirobixanthene (N)

9-(2-Phenoxyphenyl)-9-xanthenol.—To the Grignard reagent from 0.6 g. of magnesium and 7.4 g. of 2-iododiphenyl ether was added a solution of 4.9 g. of xanthone in 25 cc. of hot benzene. The mixture was refluxed on the steam-bath overnight and the precipitate filtered, washed and decomposed. The recrystallized carbinol, slightly brownish clumps of crystals, melted at 136–137°; yield, 6.3 g. No tendency toward formation of a complex with xanthone was noticed in the case of this carbinol.

Anal. Calcd. for $C_{25}H_{18}O_3$: C, 81.94; H, 4.95. Found: C, 81.72; H, 4.81. Mol. wt. (in benzene). Calcd.: 366. Found: 365.

The Spiran (IV).—Heating a solution of 3 g. of the carbinol in 15 cc. of acetic acid for three hours produced 2.2 g. of 9,9′-spirobixanthene; shining colorless needles; m. p , 283–284" (corr.).

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.18; H, 4.63. Found: C, 86.38; H, 4.86. Mol. wt. (in benzene). Calcd.: 348. Found: 349.

In this spiran there are two bridge oxygen atoms instead of one, as in xanthone. These oxygen atoms may, potentially, form so-called oxonium salts. In distinction from xanthone, in the case of the spiran, devoid as it is of C=O groups, no evidence of salt formation was noticed, neither with dry hydrogen bromide nor with perchloric acid.[17]

Spiro-9-fluorene-9′-(9,10-dihydro-anthracene) (V)

Attempts to prepare carbinols by the action of Grignard reagents from 2-iodobiphenyl and from 2-iododiphenyl ether upon anthrone were unsuccessful. The desired spirans were obtained in another way, by extending the ring closures to diphenylmethane derivatives.

2-Bromo-diphenylmethane.—2-Bromobenzophenone was reduced[18] with zinc amalgam to the corresponding diphenylmethane. The crude product was distilled and yielded a colorless liquid which neither solidified nor became viscous at 0°; b. p. 192–198° at 32 mm.; yield, 50%. A large amount also of higher-boiling material was formed during the reduction.

Anal. Calcd. for $C_{13}H_{11}Br$: Br, 32.35. Found: Br, 32.15. Mol. wt. (in benzene). Calcd.: 247. Found: 252.

9-(2-Benzylphenyl)-9-fluorenol.—An ether solution of 2-bromodiphenylmethane completely dissolved 1.21 g. of magnesium in the course of four hours of boiling. Nine grams of fluorenone was added and the mixture was refluxed overnight. The insoluble yellow product was filtered, washed with ether and decomposed. The recrystallized carbinol, large colorless prisms, melted at 132–133°; yield, 10.4 g.

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.37; H, 5.91. Mol. wt. (in benzene). Calcd.: 348. Found: 351.

The Spiran (V).—Five grams of the carbinol was dissolved in 20 cc. of boiling acetic acid and one drop of concentrated hydrochloric acid was added. The solution became deep yellow and then decolorized after a few minutes of boiling. Beautiful white needles of the spiran crystallized from the cold solution; m. p. 207°; yield, 4.0 g.

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.55; H, 5.61. Mol. wt. (in benzene). Calcd.: 330. Found: 327.

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[17] Gomberg and Cone, *Ann.*, **376,** 232 (1910).

[18] Clemmensen, ***Ber.,*** 47, 681 (1914).

Spiro-9-xanthene-9′-(9,10-dihydro-anthracene) (VI)

9-(2-Benzylphenyl)-9-xanthenol.—The carbinol was prepared from 0.6 g. of magnesium, 6.2 g. of 2-bromodiphenylmethane and 4.9 g. of xanthone; colorless needles, from a mixture of ether and petroleum ether; m. p. 146°; yield, 6.9 g.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.52; H, 5.56. Mol. wt. (in benzene). Calcd.: 364. Found: 369.

The Spiran (VI).—The spiran was obtained by heating 3 g. of the xanthenol for two hours on the steam-bath with a mixture of 10 cc. of acetic acid and 3 cc. of acetyl chloride. Colorless leaflets, m. p. 257–259° (corr.).

Anal. Calcd. for $C_{26}H_{18}O$: C, 89.85; H, 5.24. Found: C, 89,57; H, 5.25. Mol. wt. (in benzene). Calcd.: 3.46. Found: 343.

Spiro-9-fluorene-9′-(10-phenyl-9,10-dihydro-anthracene) (VII)

Since 2-bromodiphenylmethane was found to react so readily with magnesium, it was decided to attempt the preparation of a Grignard reagent from 2-bromotriphenylmethane.

9-(2-Benzhydrylphenyl)-9-fluorenol.—Our 2-bromotriphenyl carbinol melted at 104–105°.[19] The carbinol was reduced to the methane by the use of concentrated hydriodic acid; m. p. 84–85'.

After twenty-four hours of boiling, a solution of 8.1 g. of 2-bromotriphenylmethane in 50 cc. of toluene and 50 cc. of ether had completely dissolved the equivalent amount of magnesium. Toluene is essential, owing to the slight solubility of the Grignard reagent in ether alone. Fluorenone, 4.5 g., was added and the mixture was refluxed overnight. The insoluble product was filtered from the cooled solution and decomposed in the customary way; yield, 51%. The recrystallized carbinol, colorless needles, melts at 192°.

Anal. Calcd. for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 90.45; H, 5.81. Mol. wt. (in benzene). Calcd.: 424. Found: 429.

The Spiran (VII).—The corresponding spiran was obtained by boiling an acetic acid solution of the carbinol containing a few drops of concentrated hydrochloric acid until the brown color which first appeared had faded; white needles; m. p. 267–268° (corr.).

Anal. Calcd. for $C_{32}H_{22}$: C, 94.54; H, 5.46. Found: C, 94.26; H, 5.43. Mol. wt. (in benzene). Calcd.: 406. Found: 408.

Spiro-9-xanthene-9′-(10-phenyl-9,10-dihydro-anthracene) (VIII)

9-(2-Benzhydrylphenyl)-9-xanthenol.—The reaction mixture from 4.9 g. of xanthone and the Grignard reagent from 8.1 g. of 2-bromotriphenylmethane was worked up as described for the preceding carbinol. White needles from benzene–petroleum ether; m. p. 200–205° with decomposition. Analysis and molecular weight determination showed the product to be a molecular complex of xanthone with the new xanthenol, one to one.

The Spiran (VIII).—The spiran was obtained in the usual way from acetic and hydrochloric acids. Colorless needles from a mixture of xylene and acetic acid; m. p. 334–335° (corr.).

Anal. Calcd. for $C_{32}H_{22}O$: C, 90.96; H, 5.25. Found: C, 90.58; H, 5.33. Mol. wt. (in benzene). Calcd.: 422. Found: 431.

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[19] Gomberg and Van Slyke, THIS JOURNAL, **33,** 535 (1911). Tschitchibabin, ***Ber.*** 44, 456 (1911), gives it as 158°.

Spiro-9-fluorene-9′-(10,10-diphenyl-9,10-dihydro-anthracene) (IX)

9-(2-Biphenyl)-10,10-diphenyl-9,10-dihydro-9-anthranol.—A hot solution of 6 9 g. of 10,10′-diphenylanthrone[20] in 50 cc. of toluene was added to the Grignard reagent from 5.6 g. of 2-iodobiphenyl and the mixture refluxed on the steam-bath overnight. The crude carbinol was extracted with petroleum ether, which removed any biphenyl present, and was crystallized from a mixture of benzene and petroleum ether; slightly yellow clumps; m. p. 231–234° with decomposition; yield, 55%.

Anal. Calcd. for $C_{38}H_{28}O$: C, 91.16; H, 5.64. Found: C, 90.98; H, 5.76. Mol. wt. (in benzene). Calcd.: 500. Found: 497.

The Spiran (IX).—Upon boiling a solution of the carbinol in acetic acid the liquid became red-brown and deposited the spiran in glistening white needles; m. p. 363–364" (corr.); yield, quantitative.

Anal. Calcd. for $C_{38}H_{26}$: C, 94.57; H, 543. Found: C, 94.87; H, 5.43. Mol. wt. (in benzene). Calcd.: 482. Found: 494

Spiro-9-xanthene-9′-(10,10-diphenyl-9,10-dihydro-anthracene) (X)

9-(2-Phenoxyphenyl)-10,10-diphenyl-9,10-dihydro-9-anthranol.—The carbinol was obtained from 6 g. of 2-iododiphenyl ether, 0.5 g. of magnesium and 6.9 *g.* of diphenylanthrone by the method of preparation used for the preceding carbinol. The crude product was recrystallized by extraction with benzene in a Soxhlet extractor; colorless microscopic crystals, only slightly soluble in benzene or toluene, m. p. 276–278° (corr.); yield, 74%.

Anal. Calcd. for $C_{38}H_{28}O_2$: C, 88.34; H, 5.46. Found: C, 88.32; H, 5.59. Mol. wt. (in benzene). Calcd.: 516. Found: 511.

The Spiran (X.)—Boiling an acetic acid solution of the anthranol caused the formation of the spiran; minute crystals, m. p. 377–380° (corr.); yield, quantitative.

Anal. Calcd. for $C_{38}H_{26}O$: C, 91.53; H, 5 26. Found: C, 91.50; H, 5.16. Mol. wt. (in benzene). Calcd : 498. Found: 511.

Di-spiro-9,9′-di-fluorene-9″9‴-(9,10-dihydro-anthracene) (XI)

9,10-Di-(2-biphenyl)-anthraquinol.—To the Grignard reagent from 15.6 g. of 2-iodobiphenyl, 5.8 g. of anthraquinone, finely divided,[21] was added in small portions. Two hundred cc. of dry toluene was then added and most of the ether was distilled. The mixture was boiled overnight under a reflux condenser, then decomposed in the customary manner and the precipitated anthraquinol was removed by filtration. The teluene layer was evaporated and the residue of this crude anthraquinol was extracted with petroleum ether, in order to remove biphenyl from the carbinol. The amount of biphenyl (3.7 g.) corresponded to 45% of the starting iodo product and indicated a very incomplete Grignard reaction. The combined two carbinol samples were repeatedly extracted with fresh portions of alkaline sodium hydrosulfite until the liquid was no longer colored. The residue, now free from anthraquinone, was washed with water and with alcohol and thoroughly dried. The anthraquinol, very slightly soluble in the usual organic solvents, was crystallized by extraction with xylene in a Soxhlet extractor; small pearly leaflets; m. p. 353–355° (corr.) with decomposition; yield, 3.6 g., which corresponds to 25%.

Anal. Calcd. for $C_{38}H_{28}O_2$: C, 88.34; H, 5.46. Found: C, 88.50; H, 5.35. Mol. wt. (in quinoline). Calcd.: 516. Found: 509.

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[20] Haller and Guyot, *Bull. soc. chim.*, [3] **17,** 877 (1897).

[21] Kovache, *Ann. Chim.*, [9] **10,** 227 (1918).

The Di-spiran (XI).—This was obtained by heating a suspension of the above anthraquinol in a mixture of acetic acid and acetyl chloride for four hours; microscopic needles; yield, quantitative. The compound was recrystallized from quinoline; m. p. 471–474° (corr.).

Anal. Calcd. for $C_{38}H_{24}$: C, 94.96; H, 5.04. Found: C, 94.83; H, 5.04. Mol. wt. (in quinoline). Calcd.: 480. Found: 454.

Di-spiro-9,9′-di-xanthene-9″,9‴-(9,10-dihydro-anthracene) (XII)

9,10-Di-(2-phenoxyphenyl)-anthraquinol.—The procedure of preparation was similar to that used for the preceding carbinol, using anthraquinone and the Grignard reagent from 2-iododiphenyl ether. The compound was crystallized from xylene, in which it is only slightly soluble; yield, 47%; shining colorless needles; m. p. 351–353° (corr.), with decomposition.

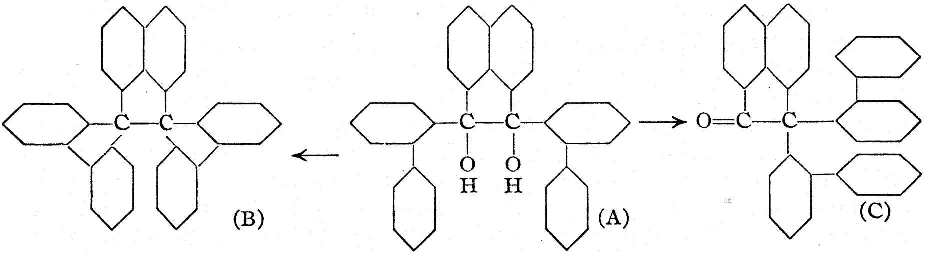
Anal. Calcd. for $C_{38}H_{28}O_4$: C, 83.18; H, 5.15. Found: C, 83.58; H, 5.21. Mol. wt. (in quinoline). Calcd.: 548. Found: 549.

The Di-spiran (XII).—The anthraquinol just described proved more refractory in eliminating water than any of the others here mentioned, a mixture of acetic acid and acetyl chloride producing no change. The di-spiran was obtained by heating 3 g. of the anthraquinol with a mixture of 20 cc. of acetic acid and 2 cc. of sulfuric acid for eight hours on the steam-bath. The substance was recrystallized from quinoline; m. p. 487490° (corr.); yield, 70%.

Anal. Calcd. for $C_{38}H_{24}O_2$: C, 89.04; H, 4.72. Found: C, 88.70; H, 4.72. Mol. wt. (in quinoline). Calcd.: 512. Found: 489.

7,7-Di-(2-biphenyl)-8-acenaphthenone

We attempted to prepare a di-spiran of another type, by dehydrating 7,8-di-(2-biphenyl)-acenaphthodiol (A). Heating in the usual way with acetic acid and hydrochloric acids did not, however, produce the expected di-spiran (B), but instead the pinacolin (C).



7,8-Di-(2-biphenyl)-acenaphthodiol.—Finely divided acenaphthoquinone, 4.55 g., and the Grignard reagent from 14 g. of 2-iodobiphenyl in toluene were refluxed overnight. The gummy product was hydrolyzed and yielded a mixture of oil and solid. The oil was removed by washing the solid several times with cold alcohol, and the solid pinacol was recrystallized several times from a mixture of benzene and petroleum ether; slightly yellow powder; m. p. 168"; yield, 3.9 g., or 32%.

Anal. Calcd. for $C_{36}H_{26}O_2$: C, 88.14; H, 5.33. Found: C, 88.54; H, 5.30. Mol. wt. (in benzene). Calcd.: 490. Found: 485.

The Pinacolin (C).—Two grams of the pinacol, when heated on a steam-bath with 10 cc. of acetic acid containing a few drops of hydrochloric acid, began to deposit crystals. After four hours the color of the solution still persisted, but no further crystallization could be observed. The product was filtered and recrystallized from a mixture of xylene and acetic acid; colorless, shining plates; m. p. 265–267° (corr.); yield, 1.5 *g*.

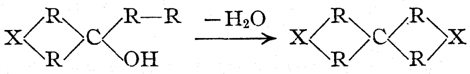
Anal. Calcd. for $C_{36}H_{24}O$: C, 91.50; H, 5.11. Found: C, 91.67; H, 5.05. Mol. wt. (in benzene). Calcd.: 472. Found: 480.

Treatment with alcoholic potash hydrolyzed the pinacolin[22] with the production of an acid, m. p. 252–254° (corr.). Apparently the rearrangement of the pinacol to the corresponding pinacolin takes place more readily than does spiran formation.

Summary

1. It has been found that the chlorides of tertiary aromatic carbinols containing the o-biphenyl group decompose spontaneously to give 9,9-disubstitution products of fluorene, which may be obtained by treating the carbinol with mild dehydrating agents.

2. This reaction has been extended to tertiary aromatic carbinols which contain, instead of the o-biphenyl group, the o-phenoxyphenyl-, o-benzylphenyl or o-benzhydrylghenyl group, respectively. The tendency toward ring closure on the part of these carbinols and carbinol chlorides has been utilized by us in preparing new spiro compounds



X is a valence, an O, a CH_2, a CH(Ph) or a $C(Ph)_2$

In all, twelve new spirans have been prepared, including two di-spirans. The spirocarbon atom has all its four valencies occupied by aryl groups—such spiro compounds being at present only little known.

The complex spirans, all beautifully crystalline, are characterized by unusually high melting points and by extreme insolubility. In accord with the views of Radulescu[4,23] the spirans were all found to be colorless.

ANN ARBOR, MICHIGAN

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[22] Beschke and Kitaj, Ann., **369**, 202 (1909).

[23] Lowenbein and Katz, *Ber.*, 59, 1377 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

A NEW METHOD OF PREPARING ACETALS. II. ACETALS OF MONOHYDRIC ALCOHOLS

BY H. D. HINTON AND J. A. NIEUWLAND

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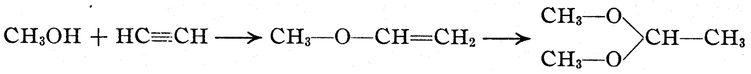
Monohydric acetals, in limited number, have been prepared by several methods, such as the method of Reichert, Bailey and Nieuwland,[1] and the standard method described by Adkins and Nissen.[2]

The process described in this paper consists in the condensation of acetylene with the monohydric alcohols into the corresponding acetals, in the presence of a new catalyst, boron fluoride in methyl alcohol with mercuric oxide, discovered by Nieuwland and Vogt[3] and recently discussed in THIS JOURNAL.

The reaction is presumed to take place in two steps:[4] (1) the formation of a vinyl ether; (2) immediate change of the vinyl ether to the acetal, in acid solution by the addition of a second molecule of alcohol, thus



$$CH_3OH + HC\equiv CH \longrightarrow CH_3{-}O{-}CH{=}CH_2 \longrightarrow \begin{matrix} CH_3{-}O \\ CH_3{-}O \end{matrix}\!\!>\!CH{-}CH_3$$

By this method all of the acetals of the monohydric alcohols, from methanol through the amyl alcohols, tertiary alcohols up to nonyl alcohol and quite a number of the phenyl alcohol acetals were made. The procedure is nearly uniform for all alcohols treated and may be illustrated by the case of iso-amyl alcohol.

Experimental

Dry acetylene gas was passed into a mixture of 200 g. of iso-amyl alcohol and 10 g. of a 63% solution of the catalyst, boron fluoride in methyl alcohol with 1 g. of mercuric oxide added. After the theoretical amount of acetylene (29.5 g.) had been absorbed, the contents of the flask was treated with a small amount of water, the acid neutralized with potassium carbonate, the acetal extracted with ether and dried over potassium carbonate. The ether was distilled off, and the solution fractionated, the products obtained being unconverted alcohol and acetal. In all cases the acetal was treated with metallic sodium to prove its freedom from hydroxylic impurities.

Fractionation was the method used to recover the acetal, and this method proved satisfactory since a number of the acetals reported in the literature were successfully prepared. Methyl alcohol acetal, isopropyl alcohol acetal, methyl propyl carbinol acetal and diethyl carbinol acetal required special methods of procedure for their recovery.

According to a process by Nieuwland (unpublished) a high-boiling aromatic fraction, xylene, was used as a solvent in the case of methyl alcohol acetal. The procedure

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[1] Reichert, Bailey and Nieuwland, THIS JOURNAL, 45, 1552 (1923).

[2] Cf. "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. III, p. 1.

[3] Nieuwland, Vogt and Poohey, THIS JOURNAL, 52, 1018 (1930).

[4] Cf. Hill and Pidgeon, *ibid.*, 50, 2718 (1928).

was as follows. After the required amount of acetylene had been absorbed, the acid in the flask was neutralized with potassium carbonate. The mixture was then distilled and to the distillate was added about one-third its volume of water, with vigorous shaking. The methyl alcohol and any aldehyde present were found in the lower layer; xylene or the higher fraction of solvent naphtha was then added and after vigorous shaking the lower water layer was separated. The upper solvent layer, containing nearly all of the acetal, was treated in a flask with 50–75 g. of potassium carbonate and 20–25 g. of anhydrous barium oxide and refluxed for ten minutes on a water-bath. It was then distilled from the xylene.

In the cases of the acetals of isopropyl alcohol, methyl propyl carbinol and di-ethyl carbinol, the ether was distilled off and the solution fractionated. The distillate containing acrtal and any alcohol was treated with calcium chloride and water to remove the alcohol. After separating the two layers, the acetal was dried over potassium carbonate, tested with metallic sodium and redistilled.

TABLE I

PREPARATIVE DATA AND PHYSICAL CONSTANTS OF COMPOUNDS (ASTERISKS DENOTE NEW COMPOUNDS)

Ethylidene compound	Taken, g.	Yield g.	%	B. p., °C.	d_4	n_D
Methyl alcohol	200	104	37	64–65	0.8494^{26}	1.3762^{26}
Ethyl alcohol	200	104	40	101–102	0.8250^{23}	1.3789^{30}
Propyl alcohol	203	90	37	146–148 5	0.8256^{26}	1.3938^{26}
Isopropyl alcohol*	200	97	40	82–84	0.7855^{25}	1.3790^{25}
Butyl alcohol	100	39.5	33 6	197–198	$0\ 8312^{26}$	1.4090^{26}
n-*Sec.*-butyl alcohol*	33	14	35	55-60 (16 mm.)	.....	1.3965^{29}
Primary isobutyl alcohol	200	102	43.4	168–169	$0\ 8123^{24}$	1.4037^{24}
n-Amyl alcohol	200	117	51 5	114–116 (16 mm.)	$0\ 8282^{26}$	1.4159^{26}
Isobutyl carbinol	200	117	51 5	210–211	0.8278^{23}	1.4175^{23}
Sec.-butyl carbinol	200	100	43 6	205–206	$0\ 8262^{25}$	1.4165^{25}
Methylpropyl carbinol*	130	45	30	120–123	0.8128^{24}	1.4069^{24}
Methylisopropyl carbinol*	59	21	30	142–145	......	1.4095^{27}
Diethyl carbinol*	78	36	40	120–121	0.8120^{27}	1.4050^{27}
Dimethyl ethyl carbinol*	200	123	53.7	90–93	0.8278^{26}	1.3965^{26}
Diethyl methyl carbinol*	...	...	..	96–99	......	1.3872^{23}
Triethyl carbinol*	...	...	..	114–116	......	1.4135^{26}
Methylethyl butyl carbinol*	...	...	..	125–128	......	1.4145^{25}
Allyl alcohol	...	...	..	90–93 (16 mm.)	......	1.4351^{28}
Tetrahydrofurfuryl alcohol*	104	37	31.6	153–155 (18 mm.)	1.3700''	1.4563^{26}
Cyclohexanol*	...	...	..	131–134 (16 mm.)	0.9560^{25}	$1\ 4651^{25}$
Benzyl alcohol*	200	102	45.5	187–189 (16 mm.)	1.0455^{25}	$1\ 5397^{25}$
Diphenyl carbinol*	..	...	..	201–202 (18 mm.)	......	$1\ 5545^{25}$
Phenyl ethyl alcohol*	122	68	50.4	204–205 (16 mm.)	1.0180^{26}	1.5302^{26}
Phenyl methyl carbinol*	...	...	..	164–166 (17 mm.)	......	$1\ 5365^{25}$
Phenyl ethyl carbinol*	70	31	40	185–187 (16 mm.)	......	1.5495^{25}
Phenyl methyl ethyl carbinol*	...	...	..	200 (14 mm.)	......	1.5801^{25}

Physical constants and analyses were determined as soon as possible after the acetal was recovered, since the acetals had a tendency to decompose on standing.

Table I shows the ethylidene compounds prepared by this new method, their physical constants and the yields obtained. Blank spaces in the table are the result of incomplete data since in these cases it was not possible to recover the acetal completely.

In explanation of this table, it might be said that Eastman purified chemicals were used, and those alcohols not obtained from the above source were prepared and purified in our laboratories, mostly by the Grignard method of making alcohols.

Tertiary butyl alcohol acetal was prepared from a technical grade of the alcohol. It was found to have the following physical constants: b. p. 78–81, d_4^{28} 0.8528, n_D^{28} 1.4050. However, technical tertiary butyl alcohol obtained from petroleum cracked gases contains isopropyl alcohol, which is difficult to remove, and it is conceivable that the acetal formation observed with this grade of tertiary butyl alcohol was due to the presence of this impurity. Attempts to make tertiary butyl alcohol acetal from the pure alcohol, melting at 25°, failed.

Triphenyl carbinol acetal was also prepared, using glycol acetal as a solvent. The reaction was rapid and vigorous, and a white solid, having the following physical constants, was obtained: b. p. 211° at 18 mm., m. p. 93°, yield 43%. It had a melting point in close proximity to triphenylmethane but the following evidence pointed to acetal formation. The crystalline structure of the acetal was uniform throughout, separating from ethyl alcohol in long needle crystals. Crystals were also obtained using benzene as the solvent. These crystals gave a melting point of 93–94°. Triphenylmethane forms a molecular compound with one molecule of benzene, melting at 75°. Molecular weight determinations showed the acetal to be approximately twice that of triphenylmethane. The analysis of the acetal closely checked the calculated amount of carbon and hydrogen. The acetal when first formed gave the characteristic aldehyde test when hydrolyzed with dilute hydrochloric acid.

If during the course of the reaction in the preparation of these acetals, the absorption of acetylene slowed down, mercuric oxide and catalyst were added to speed up the reaction. When the absorption was very rapid, the flask was cooled to prevent the decomposition of the acetal and the formation of tarry residues. In some cases the reaction proceeded slowly until about one-half of the theoretical amount of acetylene had been absorbed and then the absorption was quite rapid until the reaction was completed. It seemed that the acetal itself acted as a solvent, hastening the reaction.

The acetylene and alcohol were thoroughly dried before they entered the reaction; otherwise, the presence of water in the reaction caused the formation of acetaldehyde and crotonaldehyde, tars or resins were formed and the yield of acetal was lowered.

An interesting fact was noticed with respect to all tri-carbinols with which we experimented, *i. e.*, the acetals formed from tri-carbinols all gave boiling points below the boiling points of the alcohols. It is also noteworthy that although the formation of the Grignard reagent becomes increasingly difficult as the carbon content increases, due to the formation of alkenes, with acetals the reaction is just the reverse. Tertiary alcohols, in general, as the carbon content increased, formed acetals with increasing ease.

Furfuryl alcohol, which is a weak ring compound, decomposed during acetal formation. Tetrahydrofurfuryl alcohol, however, reacted quite smoothly and gave a very stable acetal. Cyclohexanol gave the acetal over a long period of time and also left a resin, soluble in ether. Oximes did not react, since the hydroxyl of an oxime evidently is different from the hydroxyl of an alcohol. Tetramethyldiaminobenzhydrol did not react, since the diamino groups attacked the catalyst in the solution. Benzhydrol, on the other hand, reacted quite rapidly and gave a high-boiling and stable acetal. Borneol and terpineol did not form acetals. Secondary octyl alcohol gave an acetal, but could not be recovered as it decomposed above 180° at 20 mm.

Although several of these acetals had been made by the sulfuric acid method, yet quite a number of acetals made by this new method probably could not have been made by the old method, since the sulfuric acid would have destroyed the alcohol before the reaction could have taken place. Benzyl alcohol acetal, for example, could not have been made by the sulfuric acid method for the above reason.

Acetals have a distinctive ethereal odor, which was noticed in almost all cases. The odors of the aliphatic alcohol acetals were similar, while the aromatic acetals varied. For instance, phenylethyl alcohol, used in perfumes, gave an acetal having an odor of horse-radish. The acetals also were found to be stable in the presence of alkalies, but hydrolyzed into acetaldehyde and the corresponding alcohol in the presence of dilute acids.

Nine representative acetals were analyzed, both molecular weight and carbon and hydrogen determinations being made. The molecular weight determinations were made by the boiling-point method, ethyl alcohol being used as a solvent. There were three possibilities as to the compound in considering molecular weight determinations; (1) the alcohol from which the acetal was made; (2) the vinyl ether (we found no evidence of vinyl ether formation); (3) the acetal. Since our molecular weight determinations showed that it could not be the alcohol or vinyl ether, we concluded that it was the acetal. The analyses of the same compounds came fairly close to the theoretical, as calculated, but since the alcohol and the acetal vary in percentage composition only by the weight of the acetylene, in most cases the difference in the per cent. of carbon and hydrogen of both the alcohol and the acetal was so small as to be within the range of experimental error for both.

Table II shows the data obtained on the molecular weights and analyses of the nine respective acetals.

TABLE II

ANALYTICAL DATA

		Mol. wts.		Analyses, %			
				Calcd.		Found	
Acetals	Formula	Calcd.	Found	C	H	C	H
Isoamyl alcohol	$C_{12}H_{26}O_2$	202 2	215 9	71 21	12 96	70 86	12 62
Sec.-butyl carbinol	$C_{12}H_{26}O_2$	202 2	209.0	71 21	12 96	70 67	12 48
n-Amyl alcohol	$C_{12}H_{26}O_2$	202 2	205 0	71 21	12 96	71 88	12 68
Tetrahydrofurfuryl alcohol	$C_{12}H_{22}O_4$	230 2	242.6	62 56	9 63	62 53	9 59
Triphenyl carbinol	$C_{40}H_{34}O_2$	546 3	527.8	87 86	6 27	87 92	6 07
Benzyl alcohol	$C_{16}H_{18}O_2$	242 1	255 5	79 29	7 49	80 18	7 07
Diphenyl carbinol	$C_{28}H_{26}O_2$	394 2	402 9	85 23	6 65	86 01	6 78
Phenylethyl alcohol	$C_{18}H_{22}O_2$	270.2	264.4	79 95	8 28	79 08	8 07
Cyclohexanol	$C_{14}H_{26}O_2$	226 2	224.0	74 27	11 58	73 75	11 24

Summary

1. Using a solution of boron fluoride in methyl alcohol with mercuric oxide as a catalyst, a series of acetals of the monohydric alcohols has been prepared.
2. A number of these compounds have been prepared for the first time, and cannot be made by any other known methods from acetylene or from acetaldehyde.
3. Furfuryl alcohol, oximes, borneol, terpineol and tetramethyldiaminobenzhydrol do not give acetals by this method.
4. Tertiary alcohols, in general, as the carbon content increases, give acetals with increasing ease of formation.
5. Attempts to make tertiary butyl alcohol acetal with the pure alcohol melting at 25° failed.
6. Acetals formed from tri-carbinols give boiling points below the boiling points of their alcohols.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE ULTRACENTRIFUGAL STUDY OF GELATIN SOLUTIONS

BY K. KRISHNAMURTI AND THE SVEDBERG

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The behavior and properties of gelatin solutions have been studied for a long time past. In spite of all this work, there does not appear to be any clear agreement between the views of different investigators regarding the condition of gelatin in the sol state. Several workers regard gelatin solutions as molecularly dispersed, while others maintain that they are distinctly colloids. In fact, Thomas Graham[1] himself gives gelatin as a typical example of a colloid, his chief consideration being based on the low diffusibility of the particles. Recent work[2] in this Laboratory has shown that, in spite of the very high molecular weights and the low diffusion constants of the proteins, they show certain characteristics of molecular dispersions, *viz.*, uniformity of the particles with regard to mass and size.

From a study of the scattering of light in gelatin solutions one of us[3] came to the conclusion that gelatin sols are polydispersed. The extent to which a particular sol is molecularly dispersed depends upon its concentration and temperature. At low concentrations (about 0.5%) and above 30° the sols may be regarded as molecular dispersions. When such a sol (at the isoelectric point) is cooled below 25° the intensity of the scattered light increases rapidly, indicating a marked molecular aggregation. This occurs only in a narrow region near the isoelectric point.[4] Below PH 4 and above *P*H 7.5 the Tyndall effect is practically independent of temperature, showing that in these regions of PH no aggregation of gelatin molecules takes place. In fact, it has been shown by one of us[5] that at a PH of about **3,** gelatin sols set to gels without any change of the light-scattering capacity whatsoever. It was therefore thought to be a matter of considerable interest to examine the molecular state of gelatin and see how far the above views obtained from light-scattering measurements are supported by an ultracentrifugal study of gelatin solutions. This method of investigation has the great advantage of indicating whether the sols are homogeneous or not, and, if more or less homogeneous, the approximate molecular weight can be found out.

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[1] Thomas Graham, *Phil. Trans. Roy. Soc.*, **151,** 183 (1861).

[2] Svedberg and co-workers, THIS JOURNAL, 48,430, 3081 (1926); 49, 2920 (1927); **50,** 525, 1399, 3318 (1928); **51,** 539, 550, 2170, 3573, 3594 (1929); 52, 241, 279, 701 (1930).

[3] Krishnamurti, Nature, November 2 (1929); a detailed account of the work will be published shortly.

[4] Kraemer and Dexter, *J. Phys. Chem.*, **31,** 764 (1927).

[5] Krishnamurti, *Proc. Roy. Soc.* (London), **A122,** 100 (1929).

Experimental

Material Used.—The material was leaf gelatin for photographic purposes. It was sufficiently pure for this investigation, and hence it was not further electrodialyzed; for previous researches on other proteins[6] have shown that their molecular weights are not affected by the presence of salts in the solution. Further, the presence of a small trace of salt in the gelatin was negligible since all the measurements were made in solutions of comparatively high electrolyte content.

A 3.5% stock solution of this gelatin was prepared, saturated with toluene in order to prevent bacterial growth, and stored in an ice box at 0°. Just before starting a run the solution of the required strength was prepared by diluting the warmed stock solution of gelatin with a buffer solution of the desired PH. The buffers used were sodium acetate–acetic acid mixtures over the range of *P*H 5.6 to 4.0, and mixtures of the primary and secondary phosphates over the alkaline range. The PH values of the gelatin solutions prepared were measured electrometrically. The investigation was limited to a region of *P*H between 2.5 and 7.5, as beyond these values most proteins are known to break up into smaller units. Since even in this range the gelatin solutions were not homogeneous, it was thought that the system would be rendered more complicated at higher acidity or alkalinity.

Partial Specific Volume.—The partial specific volume of gelatin was determined pycnometrically at 30 and 20°, and calculated according to the method described before.[7] The results are given in Table I. It is clear from the figures that the partial specific volume is practically unaffected by changes in the temperature, concentration and *P*H value. Further, the value of V obtained for gelatin is distinctly lower than the corresponding value for other proteins (which was found to be between 0.743 and 0.749).

TABLE I

PARTIAL SPECIFIC VOLUME OF GELATIN

Temp., °C.	Solvent	PH	Concn., %	Part. sp. vol.
30	Water	5.6	2 0	0.682
30	Water	5.6	1.0	.682
20	Water	5 6	1.0	.682
20	Acetate buffer	4.0	1.0	,685

In fact, the specific volume of gelatin in the dry state as determined by Taffel[8] is 0.744. It is of interest to note in this connection that a large contraction (probably of the solvent) takes place when gelatin is brought in contact with water. This contraction as determined by Svedberg: *viz.*, 0.059 cc. per gram of gelatin is practically equal to the difference between the specific volume of gelatin in the solid state and that in solution. It thus appears that the great divergence of the value of V of gelatin in solution from those of other proteins is due to this contraction.

Light Absorption.—The light absorption of an unbuffered gelatin solution of PH 5.6 and concn. 0.2% was determined with the Judd–Lewis

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[6] Cf. Svedberg and Stamm, THIS JOURNAL, 51, 2177 (1929).

[7] Svedberg and Chirnoaga, *ibid.*, 50, 1401 (1928).

[8] Taffel, J. Chem. *Soc.*, 121, 1971 (1922).

[9] Svedberg, THIS JOURNAL, 46, 2676 (1924).

spectrophotometer. The specific absorption coefficient is given by $\epsilon/c = 1/cd \times \log I/I_0$, where c is the concentration, d the thickness of the solution, I_0 the intensity of the light beam after passing through the solvent, and I the intensity of light after passing through the same thickness of solution. In Fig. 1 ϵ/c is plotted against the wave length of light. On comparing this curve with those of other proteins, it will be found that a steep fall occurs at about 240 $\mu\mu$ for gelatin, as for other proteins, but instead of the maximum at 276 $\mu\mu$, the curve is flat in the case of gelatin. The light absorption between 250 $\mu\mu$ and 290 $\mu\mu$, though small compared with that of other proteins, is still sufficient for the ultracentrifugal investigation.

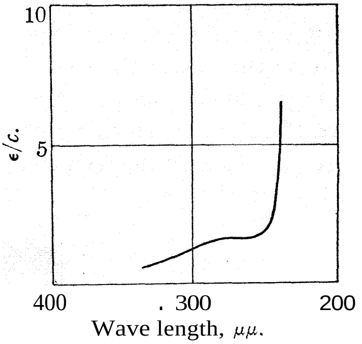

Fig. 1.—Light absorption of gelatin at PH 56.

Ultracentrifugal Investigation

A. Sedimentation Velocity Method.—This method has been described in detail in previous papers. According to this it is possible to determine the molecular weight of a protein, when its solution is a uniform dispersion. The molecular weight is given by the relation

$$M = \frac{RTs}{D\,(1 - V\rho)}$$

where R is the gas constant, T the absolute temperature, s the specific sedimentation velocity, *i. e.*, $1/\omega^2 x \times dx/dt$, V the partial specific volume of the protein, ρ the density of the solvent, x the distance from the axis of rotation, ω the angular velocity and t the time.

The values of the specific sedimentation velocity were all reduced to 20° by means of the relation $s_1/s_2 = \eta_2/\eta_1$, and the diffusion constants by means of the relation $D_1/D_2 = T_1\eta_2/T_2\eta_1$ where η is the viscosity of the solution.

The present investigation was carried out with 0.4% gelatin solutions. It was not possible to work with solutions of various concentrations, for with the more concentrated solutions there was an indication of gel formation, whereas with the more dilute ones the light absorption was not sufficient to work conveniently in the ultracentrifuge.

The determination of the molecular weights by the above method requires the knowledge of the diffusion constant. The values of D obtained in the case of heterogeneous systems like gelatin sols are not true diffusion constants, and hence it is not possible to calculate the molecular weight of gelatin by this method. The determination of the sedimentation constant under different conditions is nevertheless of great interest, since it would give an insight into the nature of gelatin solutions. A summary of all of the sedimentation velocity runs is given in Table II. It will be seen from the results that: (1) within a region of P_H between 4.6 and 6.0, the sedimentation constant obtained even with freshly prepared solutions is quite high and is not reproducible (*i.e.*, it is irregular) and corresponds to that obtained with proteins like serum globulin having an approximate molecular weight of 100,000.

(2) Within this P_H range the effect of aging on the sedimentation constant s is very marked; there is a considerable increase of s with age—the more so the nearer the solution is to the isoelectric point. This suggests an aggregation of gelatin molecules—a conclusion which is in perfect accord with the light-scattering measurements made by one of us.[3,5] In fact, the aggregation is so marked that the particles sediment almost completely in a very short time.

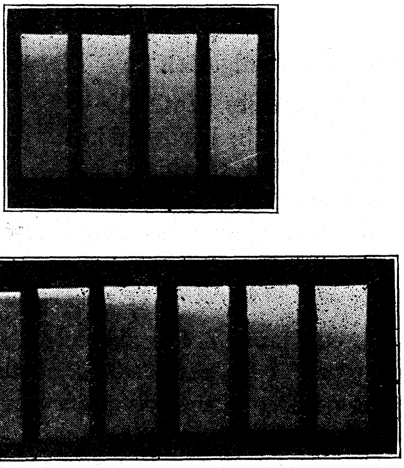

Fig. 2.—Sedimentation of 0.4% gelatin in acetate buffer in a centrifugal field about 100,000 times gravity. Upper picture: P_H 4.8, 15 min. between exposures, rapid sedimentation. Lower picture: P_H 4.0, **30** min between exposures, slow sedimentation, $s = 3.75 \times 10^{-13}$.

(3) At and below P_H 4 and also at P_H 7.5 the sedimentation constant (s) is much lower and corresponds to that of egg albumin with a molecular weight of about 35,000. Further in this region aging has practically no effect on s, thereby indicating that no aggregation of the gelatin molecules takes place. This also is in harmony with the light-scattering measurements. The marked difference between the sedimentation velocities in the neighborhood of the isoelectric point and at P_H 4 is clear from the illustrations in Fig. 2.

(4) At P_H 2.5 there is no appreciable sedimentation even at a speed of

about 41,000 r. p. m. (corresponding to a centrifugal force of about 100,000 times that of gravity), thus indicating that at this PH the gelatin molecules have been largely decomposed. This is, in fact, what one would expect in view of the very similar behavior of other proteins. It is of further interest that the range of stability on the alkaline side of the isoelectric point is much wider than on the acid side. **A** more detailed investigation is, however, necessary to settle the nature and the extent of the decomposition in solutions of high acidity and alkalinity.

TABLE II

SUMMARY OF SEDIMENTATION VELOCITY MEASUREMENTS ON GELATIN

No.	Solvent	PH	Concn., %	Sedimentation velocity ($s_{20^\circ} \times 10^{13}$) Fresh soln.	After aging	Remarks
1	Acetate buffer	4.0	0.4	3.33	...	......
2	Acetate buffer	4.0	.4	..	**3.75**	Soln. **1** kept for 2 days
3	Acetate buffer	4.8	.4	Sediments very rapidly	...	Near isoelectric point
4	KCl + HCl soln.	4.6	.4	8.10	...	......
5	Acetate buffer	5.5	.4	4.96	...	......
6	Acetate buffer	5.5	.4	..	Sediments almost completely in 30 min.	Soln. **5** kept for **2** days
7	*N*/50 KCl soln.	5.6	.4	5.92	...	A few hours after preparation of sol
8	*N*/50 KCl soln.	5.6	.4	4.99	...	......
9	*N*/50 KCl soln.	5.6	.4	..	13.42	Soln. kept overnight
10	*N*/50 KCl soln.	5.6	.4	5.69	...	......
11	*N*/50 KCl soln.	5.6	.4	..	8.30	Soln. 10 kept for 2 days
12	*N*/50 KCl soln.	5.6	.8	**3**.62	...	Forms a weak gel.
13	Phosphate buffer	7.5	.4	3.64	...	......
14	Phosphate buffer	7.5	.4	..	3.43	Soln. 13 kept for 2 days
15	KCl + HCl soln.	2.5	.4	No appreciable sedimentation	...	Gelatin probably dec. at this PH

The "diffusion constant" D as calculated by the method indicated in previous papers is a real constant only in the case of a monodisperse system but not for a polydisperse system like gelatin, where the value of D has been found to vary with time from the beginning of the run. This is clearly seen from Table III which gives the results of a typical run made with a gelatin solution at PH 5.6.

Figure **3** gives the curves showing the variation of this "apparent diffusion constant" D with time in the different runs. It will be seen from the curves that the higher the sedimentation velocity, the higher are the values of *D*, and, what is more interesting, the more steep is the time–D curve. It is clear that this apparent diffusion is caused by the blurring of the boundary which is, in this case, due to the sedimentation of the particles of different molecular weights at different velocities. This would cause a

TABLE III

RESULTS OF A TYPICAL SEDIMENTATION VELOCITY RUN MADE UPON A GELATIN SOLUTION OF P_H 5.6[a]

Concn. 0.4%; V = 0.682; ρ = 1.0; length of column of soln., 1.20 cm.; exposure time, 60 sec.; temp., 19.5°; average speed, 40,800 r. p. m.

	Sedimentation		Centrifugal	S_{20}	Diffusion		$D_{20°}$
At, sec.	*Ax*, cm.	Mean *x*, cm.	force, $\omega^2x \times 10^{-7}$	cm /sec. per cm./sec.^{2} $\times 10^{13}$	Time, sec.	Mean Z, cm.	cm.^{2}/sec. $\times 10^7$
900	0.035	4 578	8.44	4 87	1800	0.030	5.81
900	.035	4.613	8.42	4.88	2700	.045	8.72
1800	.075	4 668	8.48	5 14	4500	.080	16.4
1800	.075	4.743	8.66	5 00	6300	.120	26 2
1800	.075	4.818	8.79	4.93	8100	.150	31.8

[a] *At* is the time interval between exposures; *Ax* the distance through which the part of the boundary where the concentration is half the constant part of the solution has moved; "mean Z" is the mean of the distances on the photometer curves from the point where the concentration is 50% to the point where the concentrations are 25 and 75%, respectively, the concentration in the unchanged part of the solution being taken as 100%.

separation of the boundaries of the different molecular species. Now the interesting question arises whether the blurring is due to the presence of different chemical entities in the solution or to the presence of particles of various sizes, which represent varying degrees of molecular aggregation. It appears from the results that both are possible. In the case of gelatin

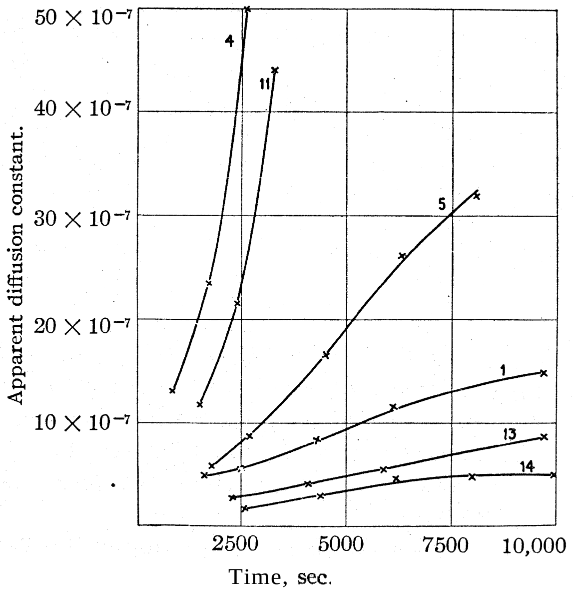

Fig. 3.—Variation of apparent diffusion constant with time of centrifuging for 0.4% gelatin solutions (the numbers of the curves refer to Table II).

solutions at PH 4.0 and 7.5, the variation of D with time is small, whereas within the region of *P*H 4.6—6.0 it is very large. The considerable increase of the sedimentation velocity of the gelatin particles and of the light-scattering capacity of gelatin sols within the region of *P*H 4.6–6.0 clearly indicates a very marked aggregation of the gelatin molecules. It is thus apparent that this causes a heterogeneity in the system and is responsible for the great increase of D with time.

It can also be seen from the curves in Fig. **3** that even with gelatin solutions at PH 4.0 and 7.5, there is an appreciable increase of "*D*" with time. Since there is no aggregation at these *P*H values, this effect is to be associated with the heterogeneity of the original gelatin solutions, *i. e.*, the existence of different molecular species in gelatin.

B. Sedimentation **Equilibrium** Method.—This method enables us to find out with greater certainty than the previous one whether the system is heterogeneous or not, and, if heterogeneous, the approximate molecular weights of the different molecular species can be calculated. The molecular weight, according to this method, is given by

$$M = \frac{2RT \ln (c_2/c_1)}{(1 - V\rho)\ \omega^2(x_2^2 - x_1^2)}$$

where R, T, V, ρ and ω have their usual meaning and c_1 and c_2 are the concentrations at distances x_1 and x_2 from the center of rotation.

This method is based on the equilibrium reached in the cell during centrifuging between diffusion and the centrifugal force. As in the case of gelatin solutions of PH between 4.6 and 6.0, the marked aggregation of the gelatin molecules causes a heterogeneity in the system, it was thought best to work at PH 4.0, where the aggregation is practically negligible. Two runs were therefore made[10] by the sedimentation equilibrium method at *P*H 4.0. The results of one of the runs are given in Table IV. The results of the two runs are plotted graphically in Fig. 4. It is clear from the results that gelatin solution is a heterogeneous system and that the values of the molecular weight determined at various distances from the center of rotation

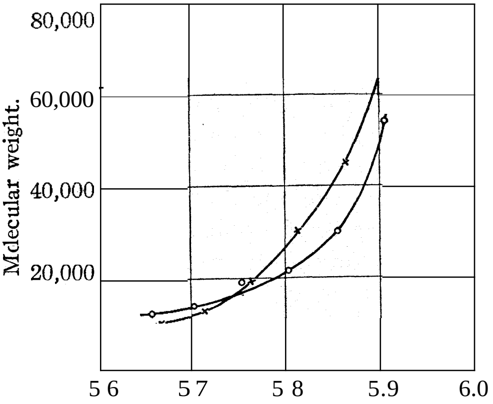

Fig. 4.—Variation of molecular weight with distance from axis of rotation for two equilibrium runs made on gelatin solutions of PH 4.0.

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[10] These two runs were made by Mr. Bertil Sjögren, to whom we desire to express our best thanks.

vary from about 70,000 to 11,000. It appears from the curves that a molecular species of about 11,000 is present to a comparatively large extent.

TABLE IV

RESULTS OF A SEDIMENTATION EQUILIBRIUM RUN MADE UPON A GELATIN SOLUTION AT PH 4

Concentration, 0.4%; acetate buffer, PH 4.0 (0.016 M in HAc and 0.004 M in NaAc); $V = 0.682$; $\rho = 1.000$; $T = 293.2$; length of column of solution, 0.42 cm.; thickness of column 0.8 cm.; distance of outer end of soln. from axis of rotation 5.95 cm.; speed 11,000 r. p. m.; standard, K_2CrO_4, $M/200$; thickness of standard cell 0.4 cm.; time of exposure 30, 60 and 120 sec.; exposures made after 40, 57 and 74 hours of centrifuging; aperture of lens F:36; optical and photographic conditions as usual.

Distances, cm. x_2	x_1	Mean concn., % c_2	c_1	No. of exposures	Molecular weight
5.94	5.89	0.606	0.417	2	73,000
5.89	5.84	.417	.332	8	44,900
5.84	5.79	.332	.286	8	29,630
5.79	5.74	.286	.260	8	19,110
5.74	5.69	.260	.244	8	12,840
5.69	5.64	.244	.232	8	10,280
5.64	5.59	.232	.222	8	9,070

From the exposures at different times it can be seen that gelatin is undergoing change during the sedimentation equilibrium run. It is therefore possible that the equilibrium does not represent exactly the same state of gelatin as did the samples which were used in the sedimentation velocity measurements.

The molecular weights of all monodisperse proteins hitherto examined (excepting the hemocyanins with molecular weights of the order of millions) have been found to be one, two, three or six times 35,000. Lower values than 35,000 have been observed for decomposition products of these proteins and also in the case of polydisperse protein systems where there was reason for believing that decomposition had taken place during the process of isolating the protein.

It therefore seems probable that the molecular species of about 11,000 is a product of hydrolysis of gelatin molecules and, in fact, it is quite natural to expect from the methods of manufacture that gelatin is a complex substance containing some of the products of hydrolysis.

On the other hand, the data so far collected do not exclude the possibility that a molecular species with a weight around 11,000 is really present in the original protein together with other species of higher molecular weights, or the possibility that 11,000 is the real molecular weight of gelatin and that the higher values represent aggregation states.

Discussion of Results

The ultracentrifugal study of gelatin solutions has been fruitful in revealing the heterogeneous nature of the sols. The measurements of the specific sedimentation velocity have shown that within a range of PH 4.6–

6.0 there is a very marked aggregation of the gelatin molecules; whereas at PH 4 and 7.5 there is practically no aggregation—a conclusion which is in complete harmony with the light-scattering measurements. It has been found that the diffusion constants calculated from the sedimentation velocity runs are only apparent, because they have been found to increase with time, which is not the case in a monodisperse system. This clearly points out the heterogeneous nature of gelatin sols even at PH 4 where there is no aggregation. The sedimentation equilibrium runs with gelatin sols at PH 4 have confirmed the above view and have shown that the gelatin solutions have different molecular species with molecular weights ranging from 70,000 to 11,000. Previous estimates of the molecular weight of gelatin have given very different values. Thus, Biltz[11] found a value of 17,000; Schryver[12] found a similar value of 17,000 to 19,000; C. R. Smith[13] from osmotic pressure measurements of isoelectric gelatin found a value of 96,000. More recently, Cohn[14] has calculated a minimal molecular weight of about 10,300 from analytical data. In view of the great divergence in the values of the molecular weight of gelatin as given by various workers, one can hardly attach great importance to the previous estimates.

It has been realized by several investigators that gelatin is a complex substance, and that it is impossible to isolate a single chemical species in gelatin. Recently, however, Schryver[15] and also Northrup and Kunitz[16] report that they have succeeded in fractionating gelatin into "soluble" and "insoluble" portions. It has not been shown definitely whether one of the fractions is not, in reality, obtained by the hydrolysis of gelatin molecules. The molecular species of molecular weight 11,000, which is present in gelatin to a large extent (as shown by the sedimentation equilibrium runs), is probably a decomposition product of gelatin. Further investigation is necessary to settle this point definitely.

The expenses connected with these experiments have been defrayed by a grant from the foundation "Therese och Johan Anderssons Minne."

Summary

1. The partial specific volume of gelatin was found to be 0.682, whereas the corresponding value for other proteins is about 0.745. The difference between the two values is equivalent to the contraction (0.059 cc./g.) which takes place when gelatin is brought in contact with water. Further, the specific volume was found to be practically unaffected by changes in temperature, concentration and PH value.

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[11] Biltz, *Z. physik. Chem.*, 91, 705 (1916).

[12] Schryver, *Biochem. J.*, 17, **487** (1923).

[13] C. R. Smith, THIS JOURNAL, 43, 1350 (1921).

[14] Cohn, Hendry and Prentiss, *J. Biol. Chem.*, **63,** *764* (1925).

[15] Schryver and Thimann, *Biochem.* **J.**, 21, 1284 (1927).

[16] Kunitz and Northrup, ***J. Gen. Physiol.***, 12, 379 (1929).

2. The light absorption of gelatin was determined by means of the Judd–Lewis spectrophotometer. It was found to be small compared to the light absorption of other proteins, and, further, in place of the maximum at 276 μμ as observed in the case of other proteins, the curve is flat in the case of gelatin.

3. The previously developed ultracentrifugal methods (both the sedimentation velocity and equilibrium methods) have been fruitful in revealing the molecular state of gelatin at different H-ion concentrations.

4. These investigations have revealed the fact that within the region of P_H 4.6–6.0 there is a very marked aggregation of gelatin molecules—the more so the nearer we are to the isoelectric point—whereas at P_H 4.0 and 7.5 there is practically no aggregation.

5. The "apparent diffusion constant" was found to increase with time. This is due to a progressive separation of the boundaries of the different molecular species, and is a clear indication of the heterogeneity of the sol. It was found that the aggregation of the particles in the region of P_H 4.6–6.0 causes a great increase in the heterogeneity of the solution.

6. Even at P_H 4, where there is practically no molecular aggregation, the sols are heterogeneous. Sedimentation equilibrium runs on gelatin solutions at P_H 4 confirm this view and show a drift in ~~the values of the~~ molecular weight from 70,000 at the bottom of the cell to about 10,000 at the top of the cell.

7. It appears probable that the molecular species with molecular weight about 11,000, which is present in the solution to a comparatively large extent, is due to the decomposition products of gelatin.

8. At P_H 2.5 there is no appreciable sedimentation in gelatin solutions even at a speed of about 41,000 r. p. m. (corresponding to a centrifugal force of 100,000 times that of gravity), thus indicating that at this P_H the gelatin molecules have been largely decomposed.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEW JERSEY COLLEGE FOR WOMEN, RUTGERS UNIVERSITY]

SEPARATION AND PROPERTIES OF THE TWO MAIN COMPOMENTS OF POTATO STARCH[1]

BY M. E. BALDWIN

RECEIVED MARCH 1, 1930 PUBLISHED JULY 3, 1930

Since starch became recognized as granules composed of two distinct parts, an outer envelope and an inner more soluble portion, various methods for the separation of these components and certain of their distinguishing properties have been recorded.

Gatin-Gruzewska[2] effected a separation by treating potato starch with dilute alkali and, after neutralization and sedimentation, decanting the dissolved fraction or "amylose" from the residue or "amylopectin." The "amylose" represented 4045% of the original starch, stained blue with iodine, and had a specific rotation of +182.4' when measured in a 0.643% solution. The "amylopectin" represented 55–60% of the starch, stained red-violet with iodine, and had a specific rotation of +221° when measured in a 0.178% solution.

Tanret[3] by treatment of potato starch with hot water, sedimentation and decantation, estimated 27% of "amylose."

Sherman and Baker[4] subjected a thin paste of potato starch, prepared at 85°, to centrifugal force and obtained about 15% in the more soluble or "β-amylose" fraction.

Samec and Mayer[5] electrodialyzed a dispersion of potato starch prepared at 120°. The less soluble or "amylopectin" fraction represented 83% of the starch, contained 0.77% of phosphorus,[6] and had a specific rotation of +195–196° in solutions concentrated by distillation. The "amylose" fraction represented 17% of the starch, contained practically no phosphorus and had a specific rotation of + 189°.

Ling and Nanji[7] fractionated potato starch by freezing a paste and, after melting the frozen mass, separating the solution of "amylose" from the undissolved residue of "amylopectin" by centrifuging. The "amylopectin" after being more completely freed of "amylose" by enzymic action had a specific rotation of +221°.

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[1] Some of the data included in this paper are taken from a dissertation, "On a 'Phosphorus-Free' Amylose from Potato Starch," by M. E. Baldwin, Columbia University, 1928.

[2] Gatin-Gruzewska, *Compt. rend.*, **146**, *540* (1908); **152**, 785 (1911).

[3] Tanret, Bull. *soc. chim.*, [4] **17**, *83* (1915).

[4] Sherman and Baker, THIS JOURNAL, 38, 1885 (1916).

[5] Samec and Mayer, *Kolloid-Chem. Beihefte*, **13**, 272 (1921).

[6] Samec, Minaeff and Ronzin, *ibid.*, **19**, 203 (1924).

[7] Ling and Nanji, *J. Chem. Soc.*, **123**, 2666 (1923).

Taylor and Iddles[8] disintegrated starch grains, previously treated with hydrogen chloride in alcohol, with ammonium thiocyanate solution, then precipitated with alcohol and subjected the precipitate to ultrafiltration or electrodialysis. They obtained 97–98% of potato starch in the dissolved fraction ("β-amylose") which had a specific rotation of 181.6 calculated as $[\alpha]_D^{25}$ from the mercury vapor line by a factor obtained from work on sucrose.

A comparison of the results of these different methods reveals discrepancies among the values reported for specific optical rotation and shows that the ratio of the two fractions obtained varies with the solvent used, the effect of strong chemicals being to increase the percentage of starch in the more soluble fraction.

The purpose of this investigation has been (1) to develop a method for the fractionation of potato starch which will make a sharp separation of the material of the outer envelope from that which makes up the interior of the grain, without subjecting the starch to strong reagents or high temperatures, also, (2) to define more rigidly and compare the products.

Experimental

The method of separation which has resulted from this work is based upon the difference in water-solubility between the two parts of the starch grain. In general, it consists of gelatinizing the grains and subjecting them alternately to a freezing process and a series of extractions, each step in the separation being carried out under such conditions as were found by experiment to be most favorable to the separation. In developing the method, series of test separations were made in which conditions of time, temperature and sequence of processes were systematically varied. The influence of each change on the separation was measured by making a comparative study of the properties of the products. Since it was known from the previous work of Gatin-Gruzewska,[2] Tanret[3] and Samec and his co-workers[5,6] that the two main components of starch differ in specific rotation, phosphorus content and color-with-iodine, these properties were used as criteria of progress. Such conditions as caused the greatest divergence in these properties were selected and trial separations continued until the properties became, for each fraction, constant. These trial separations gave experimental bases for selecting the details of the final form of the method.

The products obtained have been defined by determining the following properties: (1) specific optical rotation, (2) temperature coefficient of specific optical rotation, (3) phosphorus content, (4) color-with-iodine, (5) precipitability with alcohol, (6) precipitability with iodine in potassium iodide solution, (7) retrogradation.

[8] Taylor and Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926).

The more soluble component has been designated as β-amylose and the less soluble as a-amylose,

The starch used was obtained from mature potatoes and purified by repeated sedimentation in distilled water. The air-dry product contained 13.6% of moisture. Its gelatinization temperature was 63°. Some of the grains became swollen at 60° but in order to have every grain swollen, a temperature of 63° for two minutes was necessary.

Measurement of the Properties Used as Criteria of Progress in Developing the Method

Specific Optical Rotation.—The accuracy of the polariscope used was verified by determinations of the specific rotation of 5% solutions of pure glucose in water. These values checked the recent equilibrium value of 52.5' reported by Nelson and Beegle.[9]

Clear dispersions of starch and of a-amylose were prepared for use in the polariscope by heating 0.5% dispersions at 120° for one to two hours then concentrating to 2–3% by distillation under reduced pressure. Solutions of β-amylose were also concentrated to 2–3% in this way.

Optical rotations were read to 0.05' and estimated to 0.025'. The exact concentration of each dispersion was calculated from the weight of the material left after an aliquot was evaporated to dryness. a-Amylose was dried at 110°, starch and β-amylose at 100°.

Phosphorus Content.—The percentage of phosphorus in starch and in a-amylose was determined by the magnesium ammonium phosphate method[10] and the strychnine phosphomolybdate method;[11] the percentage in β-amylose by the strychnine phosphomolybdate method.

All reagents were tested for phosphorus and purified when necessary.

Samples to be analyzed were ignited with magnesium oxide according to the method used by Vozarik[12] and by Hibbard.[13] The residue was dissolved in hydrochloric acid and neutralized with ammonium hydroxide.

Manipulation of the magnesium ammonium phosphate method was checked by determinations upon Na_2HPO_4 which had been purified and dried.

The strychnine phosphomolybdate method makes use of the cloud formed when strychnine phosphomolybdate is precipitated in acid solution. According to the directions of Pouget and Chouchak[11] a known phosphate and the unknown are compared in Nessler tubes and the depth of the one which equals the whole of the other is measured. This manipulation was varied somewhat to increase the delicacy of the method. A series of aliquots of the standard was set up for comparison with a similar series of the unknown and after formation of the precipitate these two series were dovetailed. In this way two columns of percentages were obtained of which one column contained values too high and the other too low. By making the increments of the series sufficiently small, the percentage of phosphorus was determined with accuracy to the third decimal place. The amount of phosphorus used in the known series ranged from 0.00131 to 0.00393 mg.

Color-with-Iodine.—The method of Tanret[3] was used in analyzing amylose solu-

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[9] Nelson and Beegle, THIS JOURNAL, 41, 559 (1919).

[10] Fales, "Inorganic Quantitative Analysis," The Century Co., New York, **1925.**

[11] Pouget and Chouchak, *Bull. soc. chim.*, **5,** 104 (1909); **9,** 649 (1911).

[12] Vozarik. *Z. physiol. Chem.*, **76,** 426 (1912).

[13] Hibbard, *J. Ind. Eng. Chem.*, 5, 998 (1913).

tions for blue-staining and violet-staining material. This method is based upon the property ot cellulose to adsorb from water solution β-amylose but not α-amylose. Cellulose was placed in the amylose solutions and allowed to stand. At intervals of thirty minutes a portion of the liquid was removed by filtration and both the cellulose and the filtrate were tested with iodine in dilute potassium iodide solution. These tests were repeated until the color of the filtrate ceased to change. This method makes possible the detection of small amounts of either of the amyloses in solutions of the other.

The Method of Separation

Only the final form of the method is given here: two variations are included, one of which has been especially adapted to the preparation of *a*-amylose and the other to β-amylose.

Variation I. Separation of **β-Amylose.**—The details of the method with conditions so defined as to give the best preparations of β-amylose are as follows. One liter of 1.5% paste[14] is made up by pouring 15 g. of starch mixed with 100 cc. of distilled water into 900 cc. of water at 63°. The temperature of the mixture is raised to 63° with a 70"-water-bath and held there for two minutes. After standing for two hours it is frozen in thin layers in aluminum pans. Freezing is completed in ten minutes. The frozen mass is melted over a 40° water-bath and filtered through washed filter paper to give Filtrate I and a residue which is mixed with the original volume of water, heated to 55–60°, toluene added and the mixture placed in an oven at 55–60° for sixteen hours. It is then filtered and the extraction process repeated. The residue is again frozen and the extraction repeated three times or until the filtrate is no longer stained with iodine. This method yields a series of six extracts containing β-amylose and a residue consisting of the grain envelopes or α-amylose. β-Amylose in the solid form is obtained from the extracts by precipitation with alcohol or by retrogradation.

Variation II. Separation of **α-Amylose.**—The details of the method with conditions so defined as to give the best preparations of α-amylose are as follows. Four portions of 1.5% paste, 300 cc. each, are made up by mixing, for each portion, 4.5 g. of starch with 30 cc. of distilled water and pouring the mixture into 270 cc. of water at 85°. The temperature of the paste is raised to 85° over a boiling water-bath. The paste is allowed to stand for two hours and is completely frozen in ten minutes. The frozen mass is melted and filtered. The residue is suspended in 8 liters of distilled water at room temperature and allowed to settle for twenty hours. The extract is removed by decantation. This process is repeated with water at room temperature, then at 85° and three times at room temperature or until the filtrate no longer stains with iodine. The grain envelopes, a-amylose, may be suspended in water and kept under toluene or dried and ground to a fine powder.

Quantitative Measurements of the Fractions Obtained by the Two Variations of the Method

Separations for the purpose of measuring quantitatively the fractions obtained were carried out parallel with separations used for preparing material for analyses. The data obtained are given in Tables I and II.

Some Details from the Experimental Development of the Method.—Except for the more significant observations and conclusions, the data from the individual series of test separations which led to the above method have been omitted.

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[14] The word paste is used to mean gelatinized grains suspended in water.

TABLE I

VARIATION I FOR PREPARATION OF β-AMYLOSE

		Separation No. I 400 cc. 1.5% paste		Separation No. II 200 cc. 1.5% paste		Separation No. III 200 cc. 1.5% paste	
Filtrate number	Process by which filtrate was obtained	Milli-grams of amylose	Amylose, percentage of starch	Milli-grams of amylose	Amylose, percentage of starch	Milli-grains of amylose	Amylose, percentage of starch
1	Freezing 63° paste	683.2	11.39	330.1	11.00	284.4	9.48
2	Extracting at 55–60°	150.0	2.50	83.3	2.77	113.0	3.77
3	Extracting at 55–60°	27.2	0.45	22.6	0.75	30.7	1.02
4	Freezing residue	13.6	.23	10.3	.34	8.7	0.29
5	Extracting at 55–60°	21.7	.36	10.5	.35	12.7	.42
6	Extracting at 55–60°	12.8	.21	7.2	.24	9.4	.31
7	Extracting at 55–60°	12.2	.20	5.5	.18	6.8	.23
8	Extracting at 55–60°	9.7	.16	2.5	.08	3.0	.10
		930.4	15.50	472.0	15.71	468.7	15.62

TABLE II

VARIATION II FOR PREPARATION OF α-AMYLOSE

		Separation No. I 100 cc. 1.5% paste		Separation No. II 100 cc. 1.5% paste	
Filtrate number	Process by which filtrate was obtained	Milli-grams of amylose	Amylose, percentage of starch	Milli-grams of amylose	Amylose, percentage of starch
1	Freezing 85° paste	193.7	12.91	156.1	10.41
2	Washing at room temperature	54.1	3.61	87.0	5 80
3	Washing at room temperature	8.6	0.57	9.7	0.65
4	Washing at 85°	45.7	3.05	39.5	2.63
5	Washing at room temperature	19 3	1 30	18.1	1.21
		321.4	21.44	310.4	20.70

Microscopic Study.—The gelatinized grains of potato starch when first stained with iodine were violet. After a few seconds the color deepened and changed to blue. If the grains were crushed under a cover glass when first stained they appeared as burst sacs, stained violet, from which a blue-stained liquid had poured forth. If swollen, unbroken grains were frozen, then melted, they appeared as long fibers or collapsed sacs, floating in a liquid. The sacs stained violet; the liquid, blue. The expansion of the water with change of state during freezing exerted a pressure upon the grains which forced out the inner liquid. The collapsed sacs, when placed in warm water, became swollen for a second time and if they were ruptured by crushing, a liquid poured forth. This reswelling of the grains, crushed by freezing, to give a round sac containing a liquid showed that freezing did not rupture the sac. It was not necessary to rupture the sac in order to obtain from the grains the β-amylose fraction.

If gelatinized grains were allowed to stand in water, β-amylose passed slowly from the interior of the grain into the surrounding liquid. The grain sacs behaved as dialyzing membranes through which the β-amylose passed. β-Amylose could thus be obtained by soaking the grains after gelatinization although freezing hastened and helped complete its removal.

Influence of Change of Conditions.—Trial separations showed that in order to make a sharp separation it was necessary to control: (1) the temperature of gelatinizing the grains, (2) the time required for freezing the paste, **(3)** the temperature of extracting the grains.

Temperature of Gelatinizing the Grains.—An illustration of the trial separations used to develop the method is given in Table III, where the temperature to which the grains were heated in making the paste was the condition varied.

TABLE III

INFLUENCE OF TEMPERATURE OR GELATINIZING THE GRAINS

Temp., °C.	Properties of material extracted Phosphorus content	$[\alpha]^{20}_{D}$	Color-with-iodine[a]
63	0.038% of extract	188.8	Blue, no violet detected
	0.0009% of precipitate[b]	189.1	Blue, no violet detected
		189.0	
75			Blue, trace of violet
85	0.049% of extract	191.6	Blue, violet present
		190.8	
		191 **3**	
100			Blue, violet in large amount

[a] Colors were analyzed by Tanret's method. [b] The solid separating from solution on standing contained 0.0009% of phosphorus; the filtrate from this solid contained free phosphate.

From the data in this table it was learned that the material extracted at 63° had a blue color with iodine, which according to Tanret's method of analysis contained no violet-staining material, was practically phosphorus-free, and had an $[\alpha]^{20}_{D}$ of $+189°$. If higher temperatures were used in gelatinizing the grains, the phosphorus content and specific rotation increased, while violet-staining material was found present.

Time Required for Freezing the Paste.—Microscopical observations indicated that during the freezing, retrogradation[15] took place and that the longer the time required for freezing the larger the amount of material which retrograded. This conclusion was verified by quantitative experiments. The precipitate which formed during the more rapid freezing consisted of finer particles which appeared as perfect spheres when magnified, while that obtained with slower freezing was made up of coarser particles which appeared as larger spheres and conglomerates of spheres.

The ease with which retrograded amylose was dissolved and completely extracted from the grain sacs decreases as the size of the particles increased. When only ten to twenty minutes had been required for freez-

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[15] The term ***retrogradation*** is used to mean the separation of the material from solution as a solid, on standing.

ing, the precipitate passed into solution as soon as the temperature was raised to 55°. In cases where freezing required several hours, the precipitate was so coarse that several days at 55–60' were insufficient for its solution.

From the experiments on retrogradation during freezing and upon the character and solubility of the precipitate, it was concluded that shortening the time interval during which β-amylose was held at a low temperature greatly facilitated the complete removal of β-amylose from the grain sacs. Therefore, the practice of freezing the paste completely in ten minutes and melting it immediately over warm water was adopted. The material was thus subjected to a low temperature for not more than twenty minutes.

The Temperature of Extracting **β-Amylose** from the Grains.—A detailed study of extracts made at different temperatures led to the following conclusions: at temperatures from 20 to 30° retrogradation of β-amylose took place within the grain sac and made its removal incomplete; at temperatures above 75° the solvent action of water on the α-amylose became appreciable. **A** temperature from 55–60' was found to be most favorable to the separation.

Properties of the Products, *a*- and **β-Amylose**

Specific Optical Rotation in Aqueous **Solution.** Starch.—The temperature at which different investigators prepared clear dispersions of starch in water has been reported variously from 120 to 150°. A study of this variable upon the specific rotation of starch was considered necessary as a basis for establishing conditions for further work. In preparing dispersions for this purpose it was found that the greater the concentration, the higher the temperature and longer the time required to form dispersions clear enough for use in the polariscope. To obtain clear dispersions at a relatively low temperature and in a short period of heating, they were made up containing 0.5% starch and after heating in the autoclave, were concentrated to 2 to 3% by distillation under reduced pressure. The specific rotations of aqueous starch dispersions prepared at temperatures from 120 to 135' are given in Table IV.

TABLE IV

SPECIFIC OPTICAL ROTATION OF STARCH

Temperature and duration of heating dispersion	$[\alpha]_D^{\text{room temp.}}$ Determination No. I	No. II	$[\alpha]_D^{20}$ Determination No. I	No. II
0.5 hour at 120°			193.8	194.1
1 hour at 120°	194.0		194.2	194.3
1 hour at 125°	194.2		193.9	194.3
1 hour at 130°			192.1.	192.8
1 hour at 135°	189.5	189.5		

The data in Table IV show that heating the dispersion at a temperature of 130° or higher caused a decrease in specific rotation; heating at 120 or 125° for one hour caused no decrease. Therefore, the temperature of 120° was selected for later determinations. The $[\alpha]^{20}_{D}$ values for starch ranged from +193.8 to +194.3° with an average of +194.1°.

a-Amplose.—This fraction was prepared for the autoclave by boiling **0.5%** suspensions with vigorous stirring until the grain sacs were broken into fine particles that settled very slowly. The suspensions were heated for one to two hours at 120° and concentrated to 2–3% by distillation under reduced pressure. Determinations upon different preparations are given in Table V. The $[\alpha]^{20}_{D}$ values for a-amylose (prepared by Variation II of the method) ranged from +195.1 to +195.7° with an average of +195.5°.

β-Amylose.—The solutions of β-amylose used for rotation reading were the first filtrates (Filtrate I) obtained in the separation. Filtrates from later steps in the separation were so dilute that during the time required to concentrate them, retrogradation took place. The first filtrates contained **0.1** to **0.4%** of β-amylose. They were concentrated to 2–3% before direct readings were taken. Determinations upon different preparations are given in Table V. The $[\alpha]^{20}_{D}$ values for β-amylose (prepared by Variation I of the method) ranged from +188.8 to +189.6°, with an average of +189.3°. The specific rotation of β-amylose was found to be unaltered by previous heating for one hour at 120°.

TABLE V

SPECIFIC OPTICAL ROTATION OF THE AMYLOSES

α-Amylose				β-Amylose			
Prepared by Variation I		Prepared by Variation II		Prepared by Variation I		Prepared by Variation II	
B5	195.6	C1	195.6	B1	189.6	C3	190.8
B5	195.1	C3	195.4	B2	189.1	C4	191.6
B6	195.5	C4	195.2	B3	189.6	C5	191.3
337	195.7			B4	188.8		
				B8	189.3		
				339	189.2		

TABLE VI

EFFECT OF TEMPERATURE UPON SPECIFIC OPTICAL ROTATION

Starch			β-Amylose			α-Amylose		
Dispersion no.	Temp. of direct reading, °C.	$[\alpha]_D$	Prepn. no.	Temp. of direct reading, °C.	$[\alpha]_D$	Prepn. no.	Temp. of direct reading, °C.	$[\alpha]_D$
11	17.5	197.3	B8	20.0	189.3	B5	20.0	195.6
12	20.0	194.3	B9	20.0	189.2	B10	20.0	195.7
16	20.0	194.3	B9	21.25	188.9	C3	20.0	195.4
12	21.0	193.3	B10	21.50	189.4	B5	21.0	194.2
16	21.5	193.0	B8	22.50	189.0	B5	21.5	193.5
11	24.5	189.4	B8	25.00	188.7	B5	22.0	193.1
11	28.5	185.8	B9	25.50	188.3	C3	23.0	191.8
11	32.75	181.3	B8	27.50	188.3	B5	23.5	191.5
			B9	33.50	187.3	B10	26.5	187.5
						B5	27.75	185.6
						B10	30.00	183.6

Effect of Temperature upon **Specific** Optical Rotation.—Determinations of specific rotation were made at different temperatures from **20** to 30° and the data are given in Table VI.

From these data in Table VI it may be seen that when the direct rotation readings are made at different temperatures the $[\alpha]_D$ values fur starch and its components decrease as the temperature increases. Expressed as formulas these data become

[a]',of **starch** = *214.2* – $1.00t$ (t = 20–30°)
$[\alpha]^t_D$ **of** β-amylose = *191.9* – $0.13t$ (t = 20–30°)
[a]',of **a-amylose** = *220.1* – $1.23t$ (t = 20–30°)

The variation per degree in the $[\alpha]_D$ value is about ten times as great for a-amylose as for β-amylose. This difference between the **amyloses** is expressed graphically in Fig. 1.

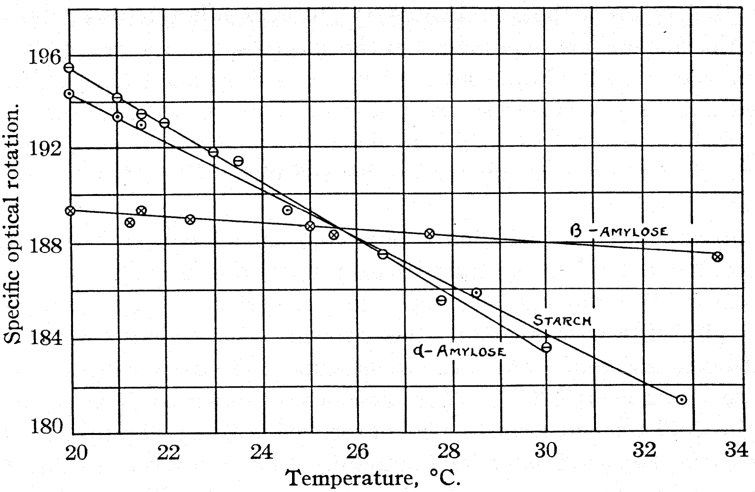

Fig. 1.—Effect of temperature upon specific optical rotation.

Phosphorus Content. Starch.—Determinations of the phosphorus in this sample of potato starch, by the magnesium ammonium phosphate method, gave 0.0691, 0.0696 and 0.0694%; by the strychnine **phosphomolybdate** method, 0.069% ± 0.0005.

α-**Amylose.**—Determinations of the phosphorus in a-amylose by the magnesium ammonium phosphate method gave 0.077 and 0.075%. Determinations on several samples by the strychnine phosphomolybdate method each gave 0.076% ± 0.0005.

β-**Amylose.**—Determinations of phosphorus in β-amylose were made by the strychnine phosphomolybdate method after it had been checked against the magnesium ammonium phosphate method. Samples of β-amylose were obtained in the solid form by precipitation with alcohol and by retrogradation. Samples of precipitated β-amylose contained 0.19% phosphorus, of retrograded amylose 0.006 to 0.0009%, the percentage decreasing with the speed of retrogradation, which increased with decrease of temperature.

The phosphorus in the two fractions, a- and β-amylose, does not represent the total phosphorus of the original starch; the remainder was found as free phosphate after precipitation or retrogradation of β-amylose.

Color-with-Iodine.—The color which a-amylose solutions developed on addition of iodine in potassium iodide solution varied with the amount of iodine, as had been noted previously by Samec and Mayer.[5] Small amounts of iodine, added either to the hydrated grain sacs or their clear dispersions, produced a light blue color which changed on further addition of iodine through violet to red-violet. In order to see whether the blue color which first develops could be detected in the presence of the red-violet, the region of the complementary absorption bands was determined. When the dispersions were placed in the spectroscope and successive additions of iodine made, the absorption band passed from left to right, through the red and orange region to the yellow, yellow-green. From the results it may be concluded that the blue color which first developed disappeared and was not covered up by the deeper red-violet formed with increased amounts of iodine.

β-Amylose gave with iodine a blue color in all concentrations of the amylose down to 0.0004%, and with all proportions of iodine until the yellow color of the iodine was so great as to give with the blue a green color.

Precipitability with Alcohol. **α-Amylose.**—Dispersions for use in precipitation experiments were made by heating 0.5 to 2.0% suspensions of α-amylose in water at 120°. When alcohol was added to these dispersions, until the final concentration of alcohol reached 85% by volume, no precipitation took place even after long standing. The addition of ether to the 85% alcohol mixture to give a final concentration of **34%** ether by volume caused practically complete (98–99%) precipitation of the a-amylose. The addition of sodium chloride also caused precipitation.

β-Amylose.—Filtrates obtained by Variation I of the method were used in precipitation experiments. When alcohol was added to these solutions, which contained from 0.1 to 0.4% β-amylose, until the final concentration of alcohol reached 65% by volume, precipitation of β-amylose was practically complete (98–99%).

Precipitability with Iodine.—Addition of iodine in potassium iodide solution to 4% dispersions of a-amylose did not cause precipitation. β-Amylose, in concentration of 0.1% or greater, was precipitated by iodine to give a dark blue precipitate in a clear liquid, colored faintly yellow by excess iodine. More than 99% of the β-amylose was thus precipitated.

Retrogradation.—β-Amylose retrograded slowly at low temperatures.

Filtrates from Variation I were found to yield 90–95% of the dissolved material as retrograded amylose in two weeks, although precipitation was probably incomplete at this point. Previous heating of the solution increased the speed of retrogradation.

The properties of the amyloses are summarized in Table VII.

TABLE VII

PROPERTIES OF a- AND β-AMYLOSE

	Starch, gelatinized at 63°	
	B	A
Properties	β-Amylose	α-Amylose
$[\alpha]^{20}_{D}$	189°	195.5"
Temperature coefficient of $[\alpha]^{20}_{D}$	0.13	1.23
Phosphorus content	0.0009%	0.076%
Color-with-iodine	Blue	Red-violet
Precipitability with alcohol	Precipitates, 98–99%	Does not precipitate
Precipitability with iodine	Precipitates, 99%	Does not precipitate
Retrogradation[b]	Retrogrades, 90–95%	Does not retrograde

[a] In absence of electrolyte. [b] The separation as a solid from solution on standing.

Discussion of the Separation

Since β-amylose is more rapidly dissolved than a-amylose and since it was obtained in a series of extracts, it was expected that if the extracts contained a-amylose as an impurity, the amount would increase progressively in the series and the properties would alter progressively toward those of a-amylose, listed under **A,** Table VII. In so far as the methods of measuring the properties could be made applicable to increasingly dilute extracts, the properties were found to be identical and the β-amylose uniform in character throughout the series.

Removal of β-amylose by repeatedly freezing and extracting grains gelatinized at 63° did not rupture the grain sacs. Sixteen per cent. of the starch was the total amount that could be obtained by these processes below the gelatinization temperature. When the residual unbroken sacs were broken into fine particles by vigorous agitation, allowed to stand in water, then filtered, the filtrate contained no dissolved material, from which it was concluded that no more material could be obtained by rupture of the sacs and that 16% was the total amount that could be obtained in solution at 63° or below.

When by gelatinizing and extracting the original starch at a higher temperature a larger amount of the starch was obtained in solution, the properties of the dissolved material diverged toward those of a-amylose, listed under A, Table VII.

The a-amylose preparations passed slowly into solution at the boiling point. By filtering before the whole sample had dissolved there were obtained a dissolved portion and an undissolved residue. The properties of these two portions were determined separately. It was expected that if the a-amylose preparations contained β-amylose as an impurity, the properties of the dissolved portion would diverge toward those of p-amylose listed under B, Table VII. The properties of both portions were identical, and the same as those listed under A, Table VII. The identity of the dissolved and the undissolved portion was evidence that the a-amylose preparations were free from β-amylose.

The temperature coefficients of specific rotation serve to explain most of the discrepancies among the values given in the literature for this analytical constant.

Comparison of the Products.—Of the six properties which were studied in order to define the amyloses, some differ numerically, others are antithetical.

While the $[\alpha]^{20}_{D}$ values of the amyloses differ by 6.5 degrees, a great difference between the amyloses is shown by the changes which this analytical constant undergoes with temperature. Between 20 and 30° the $[\alpha]^{t}_{D}$ for β-amylose is $191.9 - 0.13t$, that for a-amylose is $220.1 - 1.23t$. Thus the temperature coefficient of a-amylose is about ten times that of β-amylose.

α-Amylose is a phosphorus-bearing compound while β-amylose is "phosphorus-free."

In their behavior toward alcohol and iodine as precipitants and in regard to retrogradation, the amyloses are antithetical.

Summary

This method for the fractionation of potato starch effects the separation of the outer envelope (a-amylose) from the inner more soluble portion (β-amylose) without subjecting the material to contact with strong reagents or high temperatures. It is based upon their difference in water-solubility and consists of gelatinizing the grains, then subjecting them alternately to a freezing process and a series of extractions, each step being carried out under such conditions as were found by experiment to be most favorable to the separation. During the separation the sacs act as dialyzing membranes toward p-amylose and are not ruptured by freezing.

In developing the method, series of trial separations were carried out under systematically varied conditions and the effect of each change on the properties of the products was measured. Data from these experiments showed that the trial separations were continued until the properties, which diverged under increasingly more favorable conditions, finally ceased to diverge and became constant for each fraction. A sharp separation of the amyloses was thus indicated.

The method separates a phosphorus-bearing (a-amylase) from a "phosphorus-free" (β-) amylose which contrast strongly in their temperature coefficients of specific optical rotation and are antithetical with regard to retrogradation and toward alcohol and iodine as precipitants. A comparison of the properties of the products thus supplies additional evidence that the method effects a sharp separation of the amyloses.

β-Amylose has an $[\alpha]_D$ value at 20° of 189" which varies with the temperature according to the formula $[\alpha]_D^t = 191.9 - 0.13t$. It is practically free from phosphorus, gives a blue color with iodine which according to Tanret's method of analysis is free from violet, is precipitated by alcohol and by iodine, and retrogrades. The speed of retrogradation is increased by previous heating of the solution. β-Amylose represents 16 ± 1% of the original starch.

α-Amylose has a $[\alpha]_D^t$ value at 20° of 195.5' which varies with temperature according to the formula $[\alpha]_D^t = 220.1 - 1.23t$. It contains 0.076% of phosphorus, gives a red-violet color with iodine which according to Tanret's method of analysis is free from blue, it is not precipitated by alcohol in absence of electrolyte, or by iodine; it does not retrograde. It represents 84 ± 1% of the original starch.

The specific optical rotation of potato starch is expressed by the formula $[\alpha]_D^t = 214.2 - 1.00t$. Heating starch dispersions at 130° or above causes a decrease in the $[\alpha]_D$ value.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND AND THE HYGIENIC LABORATORY, UNITED STATES PUBLIC HEALTH SERVICE][1]

THE CHEMISTRY OF ORGANIC GOLD COMPOUNDS. I. AUROUS CHLORIDE CARBONYL AND A METHOD OF LINKING CARBON TO CARBON

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In the course of our systematic investigation of organic gold carbon compounds, we became interested in the theoretical aspects of the type of organic radicals which might form stable compounds with monovalent gold. In view of the fact that at that time our only method of preparing gold carbon compounds was by the Grignard reagent, we were naturally led to a search for some monovalent gold compounds which might be soluble in organic solvents. The literature revealed none. A method of attacking this problem was suggested by the fact that the carbonyl of platinous chloride dissolves in organic solvents. Accordingly, we decided to investigate the action of carbon monoxide with gold salts.

Previous **Work.**—The action of carbon monoxide on a water suspension of aurous chloride leads to the formation of a colloidal gold solution.[3]

[1] **Published by permission of the Surgeon General,**

[2] **This work was done in 1925 and submitted to the Graduate School of the University of Maryland in partial fulfilment of the requirements for the doctorate degree in 1926.**

[3] Donau, *Monatsh.*, 26, 525 (1905); *ibid.*, 27, 71 (1906).

Under anhydrous conditions this reaction was studied by Diemer,[4] who records that aurous chloride is decomposed into metallic gold and phosgene when heated in a stream of carbon monoxide, However, it was thought advisable to repeat his experiments at low temperatures.

When dry auric chloride was placed in a U-tube, immersed in a bath heated to 100° and dry carbon monoxide passed through the tube, a volatile gold carbon compound was formed which distilled to some extent into the receiver. Upon passing carbon monoxide over dry auric chloride one observes that the auric chloride is converted into yellow aurous chloride, which then reacts with more carbon monoxide to give the gold carbonyl compound. The same gold carbon monoxide product is formed whether one starts with aurous or auric chloride. When auric bromide was used only a small amount of crystals was formed, while with aurous iodide no combination took place.

The compound aurous chloride carbonyl was prepared by us in March, 1925. Later in the same year the preparation of the same compound was reported by Manchot and Gall.[5] The observations of these investigators regarding the optimum temperature for the dry method of preparing this compound, and the fact that either aurous or auric chloride gave the same product, are in accord with our experience. Fortunately, however, our investigation covers phases in the preparation and study of the properties of this interesting compound not touched upon by these investigators, so that no overlapping of effort has occurred. We naturally consider the priority of publication of Manchot and Gall as entitling them to the credit of having discovered this compound.

Methods of Preparation of Aurous Chloride Carbonyl

A. Action of Carbon Monoxide upon Dry Aurous or Auric Chloride.—**A** series of experiments was performed in order to ascertain the optimum condition for the preparation of aurous chloride carbonyl. The results are summarized in Table I.

As may be seen from Table I, the yields of aurous chloride carbonyl were best when a rapid stream of carbon monoxide was used and the temperature maintained around 110°. The aurous chloride carbonyl then sublimes in the form of laminar crystals. The low yields at all times are due to the decomposition of the aurous chloride carbonyl into metallic gold, carbon monoxide and phosgene.

$$2AuCl\cdot CO \longrightarrow 2Au + CO + COCl_2$$

The rapidity with which the compound is removed from the high temperature environment influences the yield. It is quite likely that higher pressures of carbon monoxide would favorably influence the yield.

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[4] Diemer, THIS JOURNAL, 35, 550 (1913).

[5] Manchot and Gall, *Ber.*, **58B,** 2175 (1925).

TABLE I

FACTORS INFLUENCING THE YIELD OF AUROUS CHLORIDE CARBONYL FROM AURIC CHLORIDE

Temp., °C.	Gas used	Yield of aurous chloride carbonyl	Remarks
100	CO	Poor	A small amount of phosgene was formed
50	CO	Poor	Extracted aurous chloride carbonyl with benzene
100	CO	Very poor	Applied suction to distil product
120	CO	Fair	Used a rapid stream of carbon monoxide gas
110	CO	20%	A rapid stream of carbon monoxide was passed over the auric chloride. This was by far the best yield ever obtained by this method.
100	CO	Fair	A rapid stream of carbon monoxide was passed over the auric chloride
100	$HCl + CO$	Poor	. ....
100	$CO + Cl_2$	Very poor	Much phosgene formed

Of interest is the experiment in which a mixture of carbon monoxide and chlorine was passed through the tube containing the auric chloride. The object of the chlorine was to regenerate the gold formed in the decomposition of the aurous chloride carbonyl. However, we found this procedure to be a fairly good one for making phosgene, but it gave an extremely poor yield of aurous chloride carbonyl. This latter observation is in disagreement with that of Manchot and Gall,[5] who recommended the simultaneous passage of chlorine and carbon monoxide over gold chloride in the production of the carbonyl compound. No yields, however, are recorded by these investigators and no mention is made of the formation of phosgene.

B. Action of Carbon Monoxide upon Aurous Chloride or Auric Chloride in the Presence of an Inert Solvent.—Since large amounts of aurous chloride carbonyl were needed for our work and the methods described above gave only small yields, another method of preparation of this compound was attempted and found to give quantitative yields. The method of procedure is as follows.

Dry carbon monoxide is passed through a benzene suspension of aurous chloride at room *temperature*. The aurous chloride gradually dissolves. If the amount of benzene is not too large it may be noted that the yellow crystals of aurous chloride are gradually converted into the colorless crystals of aurous chloride carbonyl. The method is quantitative provided all moisture is excluded, and the aurous chloride is free from metallic gold.

The preparation of aurous chloride free from metallic gold is a rather difficult procedure since the aurous chloride is ordinarily prepared by heating auric chloride. It was desired to see, therefore, whether we could not prepare the aurous chloride carbonyl by passing carbon monoxide through a solution of auric chloride. In this case, of course, the use of benzene or any solvent which is acted upon by dry auric chloride is excluded. We found that the chlorinated hydrocarbons were admirably adapted for our purpose. Thus, by passing carbon monoxide through a solution or suspension of auric chloride in tetrachloro-ethylene at 100–140°, the auric chloride was reduced to aurous chloride, with the formation of phosgene, and the aurous chloride then combined with the carbon monoxide to give the corresponding carbonyl. In view of the fact that the solution of the aurous chloride carbonyl loses carbon monoxide very readily when heated, this affords an excellent method for preparing pure aurous chloride.

Molecular Weight and Stability of Aurous Chloride Carbonyl.—The compound aurous chloride carbonyl was shown to be monomolecular. Its molecular weight in benzene solution, as determined by the freezing point method, is 223 as compared with the calculated value of 260. This difference may be due to the presence of some phosgene in the benzene solution, or to the fact that the product AuClCO is dissociated to some extent.

$$\mathrm{AuClCO} \rightleftharpoons \mathrm{AuCl} + \mathrm{CO}$$

Pertinent to this is the observation that the solid AuClCO loses carbon monoxide *in vacuo*, leaving behind a residue of aurous chloride.

Reactions of Aurous Chloride Carbonyl with Various Reagents.—A series of qualitative and quantitative reactions of a benzene solution of aurous chloride carbonyl with various reagents is given in Table II.

TABLE II

REACTIONS OF A BENZENE SOLUTION OF AUROUS CHLORIDE CARBONYL

1 Pyridine $\longrightarrow$ AuCl·pyridine + CO
2 Hexamethylenetetramine $\longrightarrow$ $\mathrm{AuCl(CH_2)_6N_4}$ + CO
3 Aniline $\longrightarrow$ Unstable compound[6] + Au (?)
4 Dimethylaniline $\longrightarrow$ Au (?)
5 Methylamine $\longrightarrow$ Au (?)
6 Ammonia $\longrightarrow$ Au (?)
7 Urea $\longrightarrow$ No apparent reaction
8 Succinimide $\longrightarrow$ No apparent reaction
9 AgCN $\longrightarrow$ No replacement of the chlorine in the aurous chloride carbonyl
10 $\mathrm{PCl_3}$ $\longrightarrow$ $\mathrm{AuCl{\cdot}PCl_3}$ + CO
11 KI $\longrightarrow$ AuI + CO + KCl
12 $\mathrm{AuCl_3}$ $\longrightarrow$ AuCl + $\mathrm{COCl_2}$
13 $\mathrm{H_2O}$ $\longrightarrow$ 2Au + CO + $\mathrm{CO_2}$ + 2HCl
14 $\mathrm{CH_3OH}$ $\longrightarrow$ Au (?)
15 $\mathrm{C_2H_5OH}$ $\longrightarrow$ Au (?)
16 $\mathrm{C_3H_7OH}$ $\longrightarrow$ Au (?)
17 $\mathrm{C_6H_5OH}$ $\longrightarrow$ Au (?)
18 $\mathrm{CH_3COOH}$ $\longrightarrow$ No apparent reaction
19 $\mathrm{(C_2H_5)_2Hg}$ $\longrightarrow$ Au + $\mathrm{C_2H_5HgCl}$ + (?)
20 $\mathrm{(C_6H_5)_2Hg}$ $\longrightarrow$ Au + $\mathrm{C_6H_5HgCl}$ + (?)
21 $\mathrm{I_2}$ $\longrightarrow$ AuI + (?)
22 $\mathrm{Br_2}$ $\longrightarrow$ $\mathrm{AuCl{\cdot}Br_2}$ + CO

[6] In the presence of a small amount of benzene a white gelatinous precipitate is formed which gradually turns purple, liberating metallic gold.

A number of interesting facts may be noted from examination of Table II. It appears that most compounds containing a basic nitrogen, when treated with aurous chloride carbonyl, yield carbon monoxide and a double compound of aurous chloride and the base. On the other hand, substances containing amide or imide groups are not acted upon by aurous chloride carbonyl. Thus, there is no reaction with succinimide or urea.

In the class of oxygen compounds, alcohols decompose aurous chloride carbonyl into metallic gold while with acids, *i.* e., glacial acetic acid, there is no apparent reaction. This property is quite likely related to the difference in ease of oxidation of the different types of molecules.

The interaction of aurous chloride carbonyl with mercury diethyl or mercury diphenyl leads to the formation of metallic gold, the corresponding alkyl or aryl mercuric halide and undoubtedly the bis-hydrocarbons. These latter products were not sought for in these reactions, but their existence is indicated by the behavior of the Grignard reagent with aurous chloride carbonyl.

Reaction of Aurous Chloride Carbonyl with the Grignard Reagent and a Method of Linking Carbon to Carbon.—The investigation of the action of the Grignard reagent on aurous chloride carbonyl had a two-fold purpose. In the first place, it was thought possible to prepare aurous carbon compounds by this method. Secondly, it was undertaken as a part of a broader investigation under way by one of us regarding the mode of attachment of carbon monoxide in carbonyl compounds.

In all of the cases investigated the action of aurous chloride carbonyl with the Grignard reagent of various types of organic radicals led to similar results, i. e., the liberation of carbon monoxide, precipitation of metallic gold and formation of the bis-hydrocarbon. No condensation products of carbon monoxide and the Grignard reagent were formed. A huge excess of the Grignard reagent was used (5 moles) and a careful but unsuccessful search made for the possible products of condensation of carbon monoxide with the Grignard reagent. Aurous chloride carbonyl thus acts in a strikingly different manner from nickel carbonyl, for Blanchard and Gilliland[7] have demonstrated that the latter compound when treated with phenylmagnesium bromide gives triphenylmethane, triphenylvinyl alcohol, pentaphenylethane, tetraphenylethylene and a non-crystallizable oil comprising more than half of the entire product.

Aurous chloride carbonyl appears to act toward a Grignard reagent somewhat as does cupric chloride.[8] Aurous chloride also acts similarly. However, much better yields of the bis-hydrocarbons were obtained by the use of a Grignard reagent on a benzene solution of aurous chloride carbonyl

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[7] Blanehard and Gilliland, THIS JOURNAL, 48, 410 (1926).

[8] Job and **Reich,** *Compt. rend.*, 174, 1358 (1922); Reich, *ibid.*, 177, 322 (1923); Gilman and Parker, THIS JOURNAL, 46,2823 (1924).

than by the use of aurous chloride. The lower yield in the case of aurous chloride may be ascribed to the fact that aurous chloride is insoluble, that its reaction product with the Grignard reagent is sticky and insoluble. The aurous chloride is thus occluded and a large amount does not enter into reaction and may subsequently be recovered unchanged.

Mechanism of Action of Aurous Chloride Carbonyl and the Grignard Reagent.—The action of aurous chloride carbonyl or aurous chloride upon the Grignard reagent may be formulated as follows

$$AuCl{\cdot}CO + C_6H_5{\cdot}MgBr \longrightarrow Au{:}C_6H_5 + MgBrCl + CO \qquad (1)$$

$$Au{:}C_6H_5 \longrightarrow \text{decomposes into two neutral fragments} \longrightarrow Au{\cdot} + {\cdot}C_6H_5 \qquad (2)$$

$$2H_5C_6{\cdot} \longrightarrow H_5C_6{:}C_6H_5 \qquad (3)$$

Thus the tendency of monovalent gold to take one electron from the phenyl group leads quantitatively to the formation of gold and diphenyl. In contrast to this, trivalent gold tends to take two electrons from the phenyl group and consequently phenylauric dichloride decomposes not into diphenyl but into phenyl chloride[9]

$$C_6H_5:Au\genfrac{}{}{0pt}{}{:Cl}{:Cl} \longrightarrow C_6H_5Cl + AuCl$$

Upon a theoretical basis it appeared interesting to study the stability of the molecule RAu. It may be seen that if the radical R gives up the electrons readily the compounds should be extremely unstable. On the other hand, if we choose for R a strongly electronegative radical, a more stable compound RAu should be obtained. The benzyl, phenyl, o- and p-tolyl and naphthyl radicals were chosen for the investigation. These radicals, as may be seen from the Table of Electronegativity of Radicals, form a series ranging from slightly electronegative to very decidedly electronegative radicals.[10]

The experiments fully justified our expectations. Thus, when benzyl- and phenylmagnesium bromides are treated with aurous chloride carbonyl, there is an instant precipitate of gold, while the o- and p-tolyl Grignard reagents precipitate gold slowly, leading to the formation of 2,2-dimethyldiphenyl and 4,4-dimethyldiphenyl, respectively. Furthermore, the Grignard reagent from the α-naphthyl radical forms a clear red solution when treated with aurous chloride carbonyl, which does not precipitate gold until heated.[11]

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[9] Kharasch and Isbell, unpublished work.

[10] Kharasch and Marker, THIS JOURNAL, 48, 3130 (1926); Kharasch and Reinmuth, *J. Chem. Ed.*, 5, 408 (1928).

[11] The investigation is being continued using radicals more strongly electronegative than the α-naphthyl radical, *i. e.*, radicals like *p*- and o-methoxyphenyl, methoxynaphthyl, etc. It is of interest to point out that theoretically silver, copper, mercury, and other metals should form a series of organo-metallic compounds-the stability of which toward heat should increase with the increase in the electronegative character of the radicals attached to the metal. In the field of organo-mercuric compounds this prediction is well substantiated.

In the latter case, however, a reaction similar to those described above takes place, and α,α′-dinaphthyl is farmed. The yields of the *bis*-hydrocarbons are quantitative upon the basis of aurous chloride carbonyl employed. The yields of the &is-hydrocarbons recorded in the experimental part are those of the pure products. Some losses were incurred during the crystallizations of the materials or in the preparation of solid derivatives from liquids formed in the reaction.

Experimental Part

The Preparation of Aurous Chloride Carbonyl from Dry Auric Chloride.—Carbon monoxide gas, liberated by the action of concentrated sulfuric acid on formic acid, was dried by allowing it to bubble through concentrated sulfuric acid. It was then passed through a U-tube containing anhydrous auric chloride, immersed in a sulfuric acid-bath. The gases evolved were led through an empty U-tube and then through a wash bottle containing a benzene solution of aniline in order to absorb any phosgene formed as the result of the interaction of the auric chloride and carbon monoxide.

At about **45**" the first appearance of a reaction was noted. At 50° some colorless crystals began to appear in the cooler portions of the U-tube. Upon gradually raising the temperature the rate of distillation of the crystals increased, reaching a maximum between **100** and **130°**. The gold chloride slowly turned yellow and finally changed to brown, whereupon the residue was reduced to metallic gold. The yield of aurous chloride carbonyl by this method was extremely low.

Anal. Subs., **0.1222. 0.0294;** Au, **0.0926, 0.0222.** Calcd. for AuClCO: Au, 75.65. Found: Au, **75.78, 75.51.**

When thus prepared aurous chloride carbonyl is obtained in clear, colorless, laminar crystals, which frequently give a mother-of-pearl appearance. It is soluble, without decomposition, in benzene, and in anhydrous ether, while in acetone there is slight decomposition, probably due to small amounts of water contained in the acetone. It reacts with water giving a gas and metallic gold, but it dissolves in glacial acetic acid without appreciable reduction or liberation of gas.

Formation of Phosgene by the Action of Carbon Monoxide upon Auric Chloride.—The gas from the reaction of auric chloride and carbon monoxide was, as previously stated, absorbed in a benzene solution of aniline.[12]

The product of the reaction of phosgene and aniline, *i. e.*, diphenylurea (m. p. **237°**) was isolated from this mixture. For further confirmation the diphenylurea was converted into the bromine derivative, the properties of which agreed with those cited in the literature. Hence we may conclude that auric chloride and carbon monoxide react thus

$$AuCl_3 + CO \longrightarrow AuCl + COCl_2$$
$$AuCl + CO \longrightarrow AuClCO$$

A Preparation of Aurous Chloride Carbonyl in the Presence of an Inert Solvent.—Aurous chloride (**1.869** g.) is suspended in dry benzene (**50** cc.), kept at 20–30° and carbon monoxide is passed through the suspension until the yellow aurous chloride is converted into a colorless, crystalline product. Benzene is then added and the mixture very gently warmed to dissolve the crystals. Any residual solid is collected on a filter and from the filtrate most of the aurous chloride carbonyl may be precipitated by the addition of petroleum ether. The balance of the product may be obtained by evaporation of the solvent in *vacuo*. The yield is **1.990** g. or **95%** of the calculated amount.

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[12] This method for the determination of phosgene is described by André Kling and Rent? Schmutz, ***Comfit. vend.***, 168, **773 (1919).**

Anal. Subs., 0.1345: Au, 0.1017. Calcd. for $AuClCO$: Au, 75.65. Found: Au, 75.61. *Mol.* wt. Subs., 0.0552: Benzene, 5.0; *t*, 0.365". Calcd. for $AuClCO$: 260. Found: 223.

Pyridine Aurous Chloride.—Pyridine reacts in benzene solution with aurous chloride carbonyl with the evolution of a gas and the formation of a white, flocculent precipitate.

Anal. Subs., 0.1320: Au, 0.0846. Calcd. for C_5H_5NAuCl: Au, 63.24. Found: Au, 64.09.

The compound is insoluble in benzene, alcohol and water, somewhat soluble in acetone, giving white crystals on evaporation. It melts with decomposition at 92°.

Hexamethylenetetramine Aurous Chloride.[13]—The addition of a benzene solution of hexamethylenetetramine to a benzene solution of aurous chloride carbonyl results in the evolution of carbon monoxide and the separation of a white crystalline compound. The solid was collected on a filter, washed well with benzene and dried in vacuo.

Anal. Subs., 0.0656: Au, 0.0342. Calcd. for $C_6H_{12}N_4AuCl$: Au, 52.75. Found: Au, 52.14.

This compound is insoluble in alcohol, benzene and ether. It reacts slowly with water, giving a colloidal solution of gold. It is not soluble in dilute acids or alkalies. It decomposes slowly over a range of temperature, the first sign of decomposition being at 150°.

Reaction of Aurous Chloride Carbonyl with Bromine.—Bromine (0.0376 g.) dissolved in chloroform was added to a molecular equivalent (0.0712 g.) of aurous chloride carbonyl. The whole was allowed to stand for twelve hours and then the chloroform was evaporated. Upon drying to constant weight in vacuo over sodium hydroxide, the residue gave the following analysis.

Anal. Subs., 0.1065: Au, 0.0539. Calcd. for $AuClBr_2$: yield, 0.1072; Au, 50.24. Found: yield, 0.1065; Au, 50.61.

This experiment indicates that aurous chloride carbonyl reacts with one mole of bromine to give the auric halide. Therefore, none of the bromine is used in the oxidation of the carbonyl group. The analysis is of course no criterion that the compound is $AuClBr_2$. It could also be a mixture of two moles of auric bromide and one of auric chloride.

Reaction of Aurous Chloride Carbonyl with Iodine.—Aurous chloride carbonyl was treated in benzene solution with slightly more than one equivalent of iodine. A yellow precipitate of aurous iodide formed.

Anal. Calcd. for AuI: Au, 60.84. Found: Au, 61.36.

The resulting benzene solution, when treated with a slight excess of aniline, did not give any solid derivative.

The Reaction of the Grignard Reagent **with** Aurous Chloride Carbonyl.—Aurous chloride carbonyl was added drop by drop to five molecular equivalents of the Grignard reagent at room temperature. Metallic gold precipitated with all the radicals tested except α-naphthyl. In the latter case warming the mixture on the water-bath for a half hour was necessary to bring the reaction to completion. After the addition of petroleum ether and decomposition of the excess Grignard reagent with ice, followed by water and dilute acid, the ethereal solution was washed free from all water-soluble substances. Upon evaporation of the ether, the residues were usually crystallized from alcohol or other solvents, until pure compounds were obtained. Although derivatives

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[13] An auric chloride hexamethylenetetramine, $AuCl_3 \cdot C_6H_{12}N$, is described by Moschatos and Tollens, *Ann.*, 272, 277 (1893).

of the carbonyl group which could have been formed due to the interaction of the Grignard reagent and carbon monoxide were also looked for, only hydrocarbons were found. The final products of the reaction may be summarized in the equation

$$2C_6H_5MgBr + AuClCO \longrightarrow (C_6H_5)_2 + 2Au + CO$$

The reaction is probably quantitative, but there is loss in the purification of the products when small quantities of material are used. The yields recorded below are those of the pure products.

TABLE III

REACTION OF AUROUS CHLORIDE CARBONYL WITH GRIGNARD REAGENTS

Five moles of	One mole	Product	Yield, %	M. p., °C.	Remarks
Phenylmagnesium bromide	AuClCO	Diphenyl	106	70	Possibly some diphenyl formed in prepn. of Grignard
o-Tolylmagnesium bromide	AuClCO	Di-o-tolyl	61.3	Liq.	Deriv. diphenic acid, m. p. 226°
p-Tolylmagnesium bromide	AuClCO	Di-*p*-tolyl	91.5	118	
Benzylmagnesium chloride	AuClCO	Dibenzyl	70.0	52	
Naphthylmagnesium bromide	AuClCO	α,α'-Dinaphthyl	70.8	151	
Phenylmagnesium bromide	AuCl	Diphenyl	70.1	70	Some aurous chloride did not react

Summary

1. A quantitative method for the preparation of aurous chloride carbonyl is described.
2. The reactions of aurous chloride carbonyl with a variety of organic substances are described.
3. The mechanism of the action of aurous chloride carbonyl with a Grignard reagent is discussed. The intermediate formation of monovalent gold carbon compounds is postulated. The order of stability of these monovalent gold carbon compounds appears to agree with the relative order of the electronegativity of the radicals investigated.
4. A method of linking carbon to carbon is described. This method is preferable to the method in which cupric chloride is employed, for the new reagent, aurous chloride carbonyl, is soluble in organic solvents.
5. The preparation of a number of new compounds is described.

CHICAGO. ILLINOIS

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

ISOCITRIC ACID[1]

BY E. K. NELSON

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The predominating acid of the blackberry is an optically active form of isocitric acid,[2] an acid which was synthesized by Fittig,[3] and later in the form of its ester, by Wislicenus and Nassauer.[4]

The optical activity of the triethyl isocitrate obtained on fractionating the ethyl esters of the acids from various lots of blackberries was not, however, found to be constant. From six lots of blackberries esters were obtained having optical rotation ranging from -9.7 to $+14.75°$, indicating that the isocitric acid of the blackberry is a mixture of the optical antipodes in varying proportions, their racemic mixture, of course, also being present. As there are two asymmetric carbon atoms in isocitric acid, and no meso form is possible, four optically active forms and two racemic forms of the acid may exist.

The present investigation was undertaken for the purpose of comparing the natural isocitric acid with the acids synthesized by Fittig and Wislicenus and further studying the properties of the blackberry acid.

Accordingly Fittig's and Wislicenus' syntheses were repeated, resulting in the production of a quantity of synthetic isocitric acid and triethyl isocitrate.

Fittig's isocitric acid (which he obtained only in partly crystalline form, mixed with lacto-isocitric acid) was obtained in practically pure form, both with and without water of crystallization, while his lacto-isocitric acid was produced in pure form, melting sharply at 160–161°.

The triethyl ester of isocitric acid prepared by Wislicenus was reported by him to boil at 149–150° at 14 mm. This boiling point could not be confirmed. Triethyl isocitrate prepared according to Wislicenus was found to boil at 180–181° at 10 mm., which is more in accordance with what would be expected for an isomer of triethyl citrate, which boils at 170° at 10 mm.

In esterifying isocitric acid directly, it was found that partial dehydration took place with the formation of diethyl lacto-isocitrate. The presence of this ester causes a marked rise in the boiling point and in the saponification equivalent and affects the melting point of the hydrazide obtained from the triethyl ester.

Better results were obtained by treating barium isocitrate, containing one molecule of water of crystallization, with absolute alcohol containing

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[1] Food Research Contribution No. 77.

[2] E. K. Nelson, THIS JOURNAL, 47, 568 (1925).

[3] Fittig, Ann., 255, 47 (1889).

[4] Wislicenus and Nassauer, *ibid.*, 285, 7 (1895).

enough hydrochloric acid to combine with the barium and leave about 2.5% excess. The barium chloride was filtered off and the esterification completed in the usual manner, In this way the triethyl ester was prepared from Fittig's acid. It had a saponification equivalent of **635** (calcd. 609.7) and boiled at 180–181° at 10 mm., whereas the ester prepared directly from the acid had a saponification equivalent of 664.6 and distilled only partly at 219° at 10 mm.

The ester prepared by the Wislicenus method had a boiling point of 181° at 10 mm., and the saponification equivalent was 613.

It was more difficult to prepare the natural acid or its corresponding lacto-acid in crystalline form, owing to the presence of the optically active form. However, both compounds were obtaihed and checked by optical crystallographic methods[5] with the acid and lacto-acid obtained by synthesis. Attempts to resolve the synthetic acid into optically active components by the use of cinchonine, cinchonidine or brucine were unsuccessful.

Experimental

Fittig's **Synthesis.**—Fittig's synthesis of isocitric acid was carried out: *32.4* g. of sodium succinate, dried at 140°, *29.5* g. of chloral and *20.4* g. of acetic anhydride were used. The yield of trichloromethylparaconic acid was *31* g., of barium isocitrate *46.4* g., and of isocitric acid, *20* g.

The aqueous solution of isocitric acid was evaporated to a sirupy consistency. From this, on long standing, crystals were deposited. These were separated by filtration and spread on a porous plate to dry. The acid melted at about 105° but softened much below that figure; *0.3210* g. required for neutralization *43.5* cc. of $N/10$ sodium hydroxide (in ice water) and *45.1* cc. on boiling, showing the presence of a little lacto-isocitric acid. *0.4203* g. lost *0.0815* g. of water at 100° in vacuo, corresponding to *19.39%* of water (calcd. for *2.5* moles of H_2O, 20.5%). As isocitric acid is converted into lacto-isocitric acid at 100° *in vacuo,* losing $1H_2O$, *1.5* moles of water must be water of crystallization.

It was found that recrystallization from ethyl acetate gave the acid free from water of crystallization; *0.2928* g. of the acid thus recrystallized required for neutralization *44.52* cc. of $N/10$ sodium hydroxide in ice water, and the same amount on boiling, thus showing its freedom from lacto-isocitric acid; *44.52* cc. of $N/10$ sodium hydroxide represents *0.2849* g. of isocitric acid, corresponding to a purity of 99.26%. The balance is probably water and as strong drying tends to produce some lacto-isocitric acid, it was analyzed without further drying.

Anal. Subs., *0.1278, 0.1015:* CO_2, *0.1736, 0.1384;* H_2O, *0.0486, 0.0375.* Calcd. for $C_6H_8O_7$: C, 37.50; H, *4.19.* Found: C, 37.06, 37.19; H, 4.25, 4.13.

Optical Crystallographic Data.—Fittig's isocitric acid (crystallized from ethyl acetate) consists of rods and irregular fragments. Its indices of refraction are $N_\alpha = 1.519$, $N_\beta = 1.527$, $N, = 1.548$, all ±*0.003.* On the rods the extinction is straight and the sign of elongation +. The double refraction is rather strong ($N, - N_\alpha = 0.029$).

Owing to the ease with which isocitric acid loses water, changing into lacto-isocitric acid, a sharp melting point could not be obtained.

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[5] The optical crystallographic examinations were made by George L. Keenan of the Food, Drug and Insecticide Administration.

When dried *in vacuo* at 100° the isocitric acid is completely changed into lacto-isocitric acid. This product was recrystallized from boiling chloroform, in which it is sparingly soluble, and was obtained as a crystalline white substance, melting sharply at 160–161°; 0.2511 g. required 30.0 cc. of $N/10$ NaOH when titrated in ice water and 42.2 cc. in boiling water.

Anal. Subs., 0.0676, 0.0812: CO_2, 0.1016, 0.1223; H_2O, 0.0222, 0.0252. Calcd. for $C_6H_6O_6$: C, 41.37; H, 3.47. Found: C, 41.00, 41.09; H, 3.67, 3.47.

Optical Crystallographic Data.—This material crystallizes in irregular fragments without definite habit. The indices of refraction are, $N_\alpha = 1.487$, $N_\beta = 1.505$, $N_\gamma = 1.600$, all ±0.003. The optic sign is + and the double refraction is extremely strong ($N_\gamma - N_\alpha = 0.113$).

Direct esterification of Fittig's isocitric acid by refluxing with absolute alcohol containing 2.5% of hydrochloric acid led to no satisfactory result, as the resulting product distilled only partly at about 219" at 10 mm. and this had a saponification equivalent of 664.6, the calculated saponification equivalent of triethyl isocitrate being 609.7 and of diethyl lacto-isocitrate 731.4.

It is therefore evident that dehydration had occurred. In order to avoid this, 40 g. of barium isocitrate was treated with an absolute alcohol solution of hydrochloride in sufficient quantity to liberate the isocitric acid and leave a sufficient excess to carry on the esterification. After standing for some time, the barium chloride was filtered off and the filtrate refluxed in the usual manner.

In this way an ester was obtained which boiled at 180–181° at 10 mm. and had a saponification equivalent of 635, which is still high for triethyl isocitrate. In order to prepare the pure ester and through this to obtain pure hydrazides, Wislicenus' synthesis was resorted to.

Wislicenus' Synthesis.—Oxal-succinic ester, prepared and purified as directed by Wislicenus, except that it was not distilled, was reduced by sodium amalgam, As the reduction under water was slow and incomplete, dilute alcohol was used as the solvent. When the ester no longer gave a color reaction with ferric chloride, the reduction was regarded as complete and the product was extracted with ether.

The ester, left after evaporation of the ether, gave a negative ferric chloride reaction. It boiled at 10 mm. at 181°.

Anal. Subs., 0.1075, 0.0996: CO_2, 0.2044, 0.1901; H_2O, 0.0681, 0.0620. Calcd. for $C_{12}H_{20}O_7$: C, 52.17; H, 7.24. Found: C, 51.87, 52.06; H, 7.09, 6.96. Saponification equivalent: 613.5, 613. Calcd.: 609.7.

The hydrazide was prepared from Wislicenus' ester in the usual manner by mixing the solution of the ester in absolute alcohol with a moderate excess of hydrazine hydrate, warming the mixture on the water-bath, and allowing it to stand at room temperature for several days. The hydrazide was recrystallized by solution in warm water and precipitation with alcohol. Thus recrystallized it melted, with decomposition, at 199".

Anal. Subs., 0.0613, 0.1305: CO_2, 0.0693, 0.1256; H_2O, 0.0329, 0.0692. Subs., 0.0508, 0.0415; N, 14.23 cc., 11.63 cc. at 0° and 760 mm. Calcd. for $C_6H_{14}N_6O_4$: C, 30.76; H, 6.02; N, 35.89. Found: C, 30.84, 30.81; H, 6.00, 5.94; N, 35.03, 35.05.

Optical Crystallographic Data.—This material crystallizes in rods and needles. Its indices of refraction are $N_\alpha = 1.540$ (crosswise), $N_\gamma = 1.632$ (lengthwise), both ±0.003. The sign of elongation is plus and the extinction is straight.

The analysis shows a deficiency of nitrogen for isocitric trihydrazide. The hydrazide is unstable, is easily hydrolyzed by hot water, and has not been obtained in a state of absolute purity. For this reason and also because the natural acid in the blackberry is a mixture of optically active and inactive acids, too much dependence cannot be placed on the melting point of the hydrazide of the natural acid.

Identification by optical crystallographic methods is preferable, and this shows that the hydrazides of the natural and synthetic acids correspond.

The hydrazide of the synthetic acid is less soluble in cold water than the hydrazide of the natural acid, and, while optical crystallographic data agree, the presence in the natural acid of the optically active form undoubtedly influences the properties of the acid, including the solubility and melting point of the hydrazide derived therefrom.

This assumption is borne out by the fact that an ester of the blackberry acid with a low optical rotation (−0 85°) gave a hydrazide less soluble in water than esters from the natural source with higher optical activity.

An attempt to racemize the natural acid by boiling with strong sodium hydroxide solution was unsuccessful.

Preparation of Isocitric Acid from Blackberries.—In order to study the optical activity of the triethyl isocitrate prepared from blackberries and to obtain material for comparison with the synthetic acid, the acid from several lots of blackberries was studied during the summer of 1929.

One lot of dewberries was included, but as these had some blackberries mixed with them the data cannot be taken as representing authentic dewberries, although the results are practically conclusive that isocitric acid is also the predominating acid of that fruit.

For the sake of comparison the characteristics of the highest boiling ester from these blackberries and those examined previously[2] are given in Table I.

TABLE I

CHARACTERISTICS OF THE HIGHEST BOILING ESTER FROM BLACKBERRIES

Ethyl ester from blackberries		B. p., °C., at 10 mm.	α_D of ester	Sap. equiv.	M. p. of hydrazide, °C.
Lot 1	1925	175–180	− 7 75°	614	178–179
Lot 2	1925	175–178	+14.75°	...	170–172
Lot 3	1925	175–178	+13.10°	619.7	170–172
Lot 4	1929	180–181	+ 5.50"	621.3	173–174
Lot 5	1929	182–187	+ 1.60°	629	179–180
Lot 6	1929	188–190	− 9.70°	651.7	.....

Lot 5 was purchased for dewberries. The acids from Lots 4, 5 and 6 were probably dried too much before esterification, resulting in partial conversion into lacto-isocitric acid.

There are two reasons for the fact that the melting points of the hydrazides and the boiling points of the esters vary. The higher saponification equivalents indicate a certain amount of dehydration during esterification, no doubt resulting in the contamination of triethyl isocitrate with diethyl lacto-isocitrate and a consequent rise in the boiling point. The variations in the optical rotation of the ethyl isocitrate from blackberries, showing variations in dextro and levo forms with the racemic form, also has its effect on the melting points of the hydrazides and on the boiling points of the esters.

As resolution of inactive (synthetic) isocitric acid with various alkaloids was so far unsuccessful, it was sought to recrystallize the hydrazides and obtain a form that would check with the hydrazide prepared from Wislicenus' triethyl isocitrate.

From the hydrazide of the ester from Lot 5, a hydrazide was obtained on fractional crystallization which melted at 196–197°, showing no depression in melting point when mixed with the hydrazide of Wislicenus' ester melting at 199°, and which gave optical crystallographic data identical with those of the Wislicenus' ester. It may be taken as proved, therefore, that the racemic form of the isocitric acid of the blackberry is identical with the synthetic isocitric acid.

The hydrazide prepared from Fittig's isocitric acid melted at 197–198°, and also checked with the hydrazide of Wislicenus' acid on optical crystallographic examination.

The difficulty of preparing a pure, crystalline isocitric acid from blackberries which will check with the synthetic acid is due to the fact that the blackberry acid contains varying amounts of the optically active acid.

White, crystalline isocitric acid was prepared from the blackberry acid, but titration showed it to contain a very considerable amount of lacto-isocitric acid, so that it was not analyzed. However, optical crystallographic examination showed the presence in it of the inactive isocitric acid, and also showed the identity of the lacto-isocitric acid of the blackberry with synthetic lacto-isocitric acid. Optical crystallographic examination further showed the hydrazide of the inactive acid in the hydrazides from the isocitric acid obtained from several lots of blackberries.

As shown in Table I, an ester with a high optical activity will give a hydrazide with a low melting point. The identification of isocitric acid by means of its ester and hydrazide requires that the acid be not dried too much before esterification and that the hydrazide be recrystallized in order to isolate the higher-melting hydrazide of the racemic acid. Much loss will occur, however, due to hydrolysis of the hydrazide if the hydrazide is kept long in contact with warm water.

Summary

Pittig's isocitric acid and the lacto-isocitric acid resulting from its dehydration have been prepared. Synthetic isocitric acid has been prepared for the first time in relatively pure form, free from lacto-isocitric acid and the latter has been prepared in sufficient purity to give a sharp melting point.

Wislicenus' triethyl isocitrate was prepared and its boiling point found to be much higher than the figure given by Wislicenus. The hydrazide of isocitric acid was prepared from this ester, but not in absolutely pure form.

Comparison of the hydrazide of natural isocitric acid from blackberries with the hydrazide of the synthetic isocitric acid shows that the former, recrystallized until the melting point is raised to 196–197°, is identical with the latter. The evidence proves that the natural isocitric acid is a mixture of dextro and levo isocitric acid with one or the other optical anti-

pode predominating, and that the synthetic acid is the racemic form of the same acid.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

STUDIES IN THE DIPHENYL SERIES. III. SOME PHOSPHORUS DERIVATIVES OF DIPHENYL

BY DAVID E. WORRALL

RECEIVED MARCH 11, 1930 PUBLISHED JULY 3, 1930

It has been shown in previous communications[1] that 4-chlorodiphenyl condenses smoothly with arsenic and antimony chlorides in the presence of sodium. The resulting tri-arylated metalloids in general have properties similar to the corresponding phenyl compounds and are useful for the preparation of derivatives containing one, two or three diphenyl groups. The study of biphenylated substances has been extended to phosphorus, the results of which are presented in the present communication.

Tri-biphenylphosphine was obtained by the action of sodium on 4-chlorodiphenyl and phosphorus trichloride dissolved in benzene.

$$3C_6H_5C_6H_4Cl + PCl_3 + 6Na = (C_6H_5C_6H_4)_3P + 6NaCl$$

The procedure followed gave directly a yield of approximately 55% of fairly pure material. The total amount of product formed was about 75% of the theoretical. Ether[2] has been used previously in similar condensations, but the results obtained in this Laboratory indicate the superiority of benzene.

Certain differences in behavior become apparent on comparing the chemical properties of tri-biphenylphosphine with the corresponding arsenic and antimony derivatives. The heats of formation of the halides of these elements increase with rising atomic weight. Therefore it was not surprising that the halogen addition products of tri-biphenylstibine were easily formed. Tri-biphenylarsine gave more trouble and the di-iodide was not isolated. Chlorine and bromine formed addition products that separated from solution with chloroform of crystallization, as was true in the stibine series. These substances, possibly because of the presence of chloroform and insolubility in water, are much less sensitive toward moisture than the corresponding phenyl derivatives. There was every indication, using tri-biphenylphosphine, that a reaction took place with chlorine and bromine, although no apparent change was observed with iodine. Yet only oils were obtained. This failure to obtain crystalline products presumably was due to the extreme hygroscopicity of the phosphorus derivatives, followed by partial hydrolysis.

$$(C_6H_5C_6H_4)_3PBr_2 + H_2O = (C_6H_5C_6H_4)_3PO + 2HBr$$

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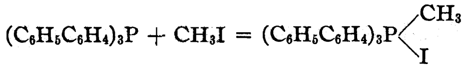
[1] Worrall, THIS JOURNAL, 52, 664 (1930).

[2] Michaelis and Reese, *Ber.*, 15, 1610 (1882).

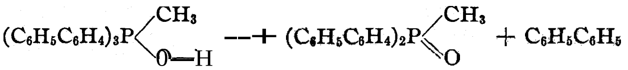
Tri-hiphenylphosphine exhibits a much stronger tendency to form salts of the ammonium type than either of the corresponding arsenic and antimony compounds. Thus methyl iodide acts not at all with tri-biphenylstibine and only slowly at elevated temperatures with tri-biphenylarsine. The reaction with tri-biphenylphosphine takes place almost instantly at room temperature.



$$(C_6H_5C_6H_4)_3P + CH_3I = (C_6H_5C_6H_4)_3P\begin{matrix} CH_3 \\ I \end{matrix}$$

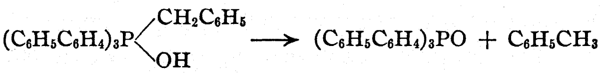
Similar reactions take place with allyl bromide and benzyl bromide, as well as ethyl chloro-acetate.

The resulting products, after treatment with silver oxide or alkali, form bases that undergo further change.[3] Thus methyl tri-biphenylphosphonium hydroxide decomposes into diphenyl and methyl di-biphenylphosphine oxide.



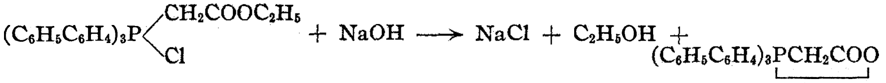
$$(C_6H_5C_6H_4)_3P\begin{matrix} CH_3 \\ O-H \end{matrix} \longrightarrow (C_6H_5C_6H_4)_2P\begin{matrix} CH_3 \\ O \end{matrix} + C_6H_5C_6H_5$$

A similar change takes place with allyl tri-biphenylphosphonium hydroxide. On the contrary, the benzyl bromide addition product changes on warming with alkali into toluene and a tri-arylated phosphine oxide.



$$(C_6H_5C_6H_4)_3P\begin{matrix} CH_2C_6H_5 \\ OH \end{matrix} \longrightarrow (C_6H_5C_6H_4)_3PO + C_6H_5CH_3$$

This same phosphine oxide is obtained from the ethyl chloro-acetate derivative under the same conditions. Tri-biphenylphosphobetaine may be isolated by working at low temperatures.



$$(C_6H_5C_6H_4)_3P\begin{matrix} CH_2COOC_2H_5 \\ Cl \end{matrix} + NaOH \longrightarrow NaCl + C_2H_5OH + (C_6H_5C_6H_4)_3\underline{PCH_2COO}$$

A striking difference in the properties of tri-arylated phosphines is the non-reactivity with phosphorus trichloride, a reaction so useful in the arsenic and antimony series (using the corresponding halide) for obtaining mono- and di-arylated derivatives.

Experimental

Tri-biphenylphosphine.—To 9 g. of granulated sodium suspended in 200 cc. of dry benzene were added 25 g. of 4-chloro-diphenyl and 6.1 g. of recently distilled phosphorus trichloride. A crystal of antimony was added and the mixture was heated to boiling under a reflux condenser. A lively reaction resulted that continued for perhaps half an hour after removal of the flame. Following this, heat was again applied for an hour and the hot mixture filtered by suction. The residue was thoroughly washed with warm benzene, the mixed filtrates concentrated to approximately 75 cc. and alcohol added to faint turbidity. A thick paste formed on stirring. It was filtered and washed thoroughly with cold alcohol; yield, 12 g. of cream-colored material pure enough for most purposes.

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[3] See Michaelis and Soden, *Ann.*, 229, 310 (1884).

Anal. Calcd. for $C_{36}H_{27}P$: P, 6.3. Found: P, 6.3.

The orange-colored filtrate from the last operation deposited a tar on further concentration containing an appreciable amount of unchanged chlorodiphenyl as well as tri-biphenylphosphine. No traces were found of diphenyl. By working up the residues, several grams of the desired product was obtained, but it was of an inferior quality difficult to purify and scarcely worth the time necessary to isolate it. The yield of tri-biphenylphosphine was not improved by longer heating during the preparation; neither was it increased by using an excess of phosphorus trichloride. Unchanged chlorodiphenyl always appeared just as in the original preparation containing an excess of sodium.

Ether was found unsuitable as a solvent in the preparation of tri-biphenylphosphine. For example, **25 g.** of chlorodiphenyl with appropriate amounts of sodium and phosphorus trichloride was mixed with **200 cc.** of **dry** ether. The ether apparently was attacked by phosphorus trichloride, for while the reaction was much more vigorous than with benzene and started without preliminary heating, the black tarry mass after evaporation of the ether contained somewhat less than three grams of tri-biphenylphosphine. Over **10** g. of chlorodiphenyl was recovered by steam distillation, while the amount of unchanged sodium present in the residues was much greater than in the preparation involving the use of benzene.

The interaction of phosphorus trichloride and chlorodiphenyl in benzene solution with sodium was decidedly sluggish, provided carefully purified and dried material was used. Several hours of heating to boiling under a reflux condenser failed to cause any tarnishing of sodium or color changes in the benzene layer, but the addition of a crystal of antimony trichloride to the hot mixture immediately caused blackening of sodium around the added crystal. Heat was also evolved as a circle of black slowly spread over the sodium and eventually the reaction was vigorous enough to cause the mixture to boil. No such effect was observed on adding a drop of arsenic trichloride. Occasionally the desired reaction did take place after the preliminary heating without the addition of antimony chloride. That the catalytic effect was not due to moisture or the mere presence of a solid was indicated by the absence of the reaction on adding pieces of porous tile moistened with water. Hydrogen, of course, was evolved and flakes of solid sodium hydroxide formed in the ether until the water was destroyed, but the sodium did not become black.

Tri-biphenylphosphine is easily soluble in hot glacial acetic acid, chloroform or benzene, separating from the latter in snow-white aggregates of tiny slender needles. It melts sharply at 172°.

Tri-biphenylphosphine Oxide.—To 5 g. of tri-biphenylphosphine dissolved in **40** cc. of **dry** chloroform was added 0.5 g. of redistilled bromine, slightly less than the chemical equivalent. Bromine was instantly absorbed while heat sufficient to cause boiling of the solvent was liberated. Crystal formation did not take place on standing and evaporation of the solvent left a yellow sirup. Undoubtedly the bromine addition product was formed, but perhaps due to partial hydrolysis from incomplete drying of the components, it was not obtained in a form suitable for analysis. The dibromide must be extremely hygroscopic as the oil puffed up like a balloon, due to the escape of hydrogen bromide, when placed in a vacuum desiccator over sulfuric acid and the air exhausted by means of a water pump. If the oil was heated in air over a flame, a crystalline residue of the oxygen compound quickly appeared as hydrogen bromide was evolved. In either case the residue was crystallized from alcohol containing a little ammonia and dried *in vacuo.* Flat needle-like crystals melting at 233–234° were obtained.

Anal. Calcd. for $C_{36}H_{27}PO$: P, 6.1. Found: P, 6.1.

While it may be unsafe to infer from the analytical data above that the substance was not tri-biphenylphosphonium hydroxide (P, 5.9), the behavior on heating, in which no change indicating loss of water was observed, substantiated the belief that it was an oxide. The oxide is much less soluble in benzene and more soluble in alcohol than tri-biphenylphosphine. Iodine did not react with tri-biphenylphosphine.

Tri-biphenylphosphine Sulfide.—Obtained by the action of carbon disulfide saturated with sulfur on tri-biphenylphosphine, as hydrogen sulfide is without action; microscopic plates melting at 241–242° with preliminary softening.

Anal. Calcd. for $C_{36}H_{27}PS$: S, 6.1. Found: S, 5.9.

Action of Phosphorus Trichloride.[4]—Three grams of tri-biphenylphosphine and 30 cc. of phosphorus trichloride were heated in a sealed tube to 225–250° for one hundred hours. A crystalline product melting at 228–230° was extracted by alcohol from the resulting black tar, apparently impure tri-biphenylphosphine oxide. The melting point was not lowered by mixing with a known sample of the oxide. No indications were obtained of the presence of monobiphenyl or di-biphenylchlorophosphines.

Tri-biphenylphosphonium Salts.—On mixing 5 g. of tri-biphenylphosphine with 25 cc. of methyl iodide, the substance promptly dissolved with considerable heat evolution. A quantitative yield of tri-biphenylphosphonium methyl iodide separated in a few minutes. Similar products were obtained by heating the phosphine for a few hours under a reflux condenser with equal amounts of the halogen derivatives listed below. Approximately 5 volumes of benzene were added in all cases to control the temperature and to facilitate the separation of the products, which are relatively insoluble in it. The phosphonium salts were recrystallized from alcohol.

TABLE I

DATA ON THE SALTS

	Cryst. form	M. p., °C.	Analyses			Remarks
			Calcd.		Found	
Methyl iodide	Sparkling plates	135–136 with foaming	20.1	I	20.0	Colors on standing
Allyl bromide	Narrow plates	195–196	13.1	Br	13.2	Forms in few minutes
Benzyl bromide	Plates	Softens above 269. Melts at 277	12.1	Br	12 2	Cryst. from alcohol and water
Ethyl chloro-acetate	Square plates	164–165	5.8	Cl	5.7	Reaction slow

These salts are easily converted into the corresponding bases by moist silver oxide or sodium hydroxide; these however, undergo further change into phosphine oxides.

Di-phenyl Methylphosphine Oxide.—Obtained by heating an alcohol solution of tri-biphenylphosphonium methyl iodide with moist silver oxide. The odor of diphenyl quickly became apparent. The mixture was then filtered and the residue extracted with a fairly large volume of hot alcohol. Lustrous slender needle-like crystals melting at 223–224° with preliminary softening separated on cooling.

Anal. Calcd. for $C_{25}H_{21}PO$: P, 8.4. Found: P, 8.5.

Di-biphenyl Allylphosphine Oxide.—Obtained from the corresponding phosphonium salt by the action of hot alcoholic potash. The product after the removal of diphenyl by steam distillation was crystallized from alcohol diluted with water. It showed a

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[4] Challenger and Pritchard observed the formation of triphenylphosphine oxide in the action of triphenylphosphine on phosphorus trichloride, J. *Chem. Soc.*, 125, 570 (1924). According to Stilp ("Dissertation," Rostock, 1910), this same oxide may form the principal product when sodium and bromobenzene react with phosphorus trichloride.

strong tendency to separate out from solution as an oil, but on standing in a cool place microscopic crystals were obtained softening above 160° and melting to a cloudy liquid at 192–193°. The analysis indicated the presence of alcohol of crystallization. This assumption is substantiated by the fact that on heating the substance in a test-tube, it melts with foaming and a combustible gas is evolved.

Anal. Calcd. for $C_{27}H_{23}PO{\cdot}C_2H_5OH$: P, 7.0. Found: P, 7.0.

The phosphine oxide may be obtained free from alcohol by drying the crystals in vacuo over sulfuric acid.

Tri-biphenyl benzylphosphonium bromide reacted differently with alcoholic potash. Toluene was set free, recognizable by its odor, while tri-biphenylphosphine oxide melting at 233–234° crystallized out in a few minutes.

Tri-biphenyl Phosphobetaine.—Tri-biphenylphosphine oxide also formed when the phosphonium salt obtained by the action of ethyl chloro-acetate was warmed with alcoholic potash. If, however, the solutions were mixed at the temperature of melting ice and subsequently poured into ice water, the betaine formed. It was washed free from alkali before recrystallization from alcohol. A pale yellow precipitate of brilliant diamond-shaped plates was obtained, melting at 109–110° with preliminary softening.

Anal. Calcd. for $C_{38}H_{29}PO_2$: P, 5.9. Found: P, 5.9.

It changes into tri-biphenylphosphine oxide on standing at room temperature.

Summary

Tri-biphenylphosphine has been obtained by the action of sodium in benzene on chlorodiphenyl and phosphorus trichloride and its chemical properties were investigated. Phosphonium salts were formed with methyl iodide, allyl bromide, benzyl bromide and ethyl chloro-acetate, which on warming in alkaline solution decomposed into phosphine oxides and hydrocarbons.

TUFTS COLLEGE, MASSACHUSETTS

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

DIARSYLS. III. DIARYLDI-IODODIARSYLS[1]

BY F. F. BLICKE AND F. D. SMITH

RECEIVED MARCH 12, 1930 PUBLISHED JULY 3, 1930

Arsenobenzenes, in the form of salvarsan and its analogs, have been made the subject of intensive investigations. Especially important from a chemotherapeutic standpoint are the oxidation products of these compounds.

It has been shown by experiments in vitro that, in general, the parasiticidal action of arseno compounds is relatively low compared with that of compounds of the arsine oxide type. Furthermore, when an arseno compound is introduced into an infected animal, there is a fairly long latent period during which there is no evidence of any parasiticidal action.

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[1] This investigation was made possible by the generous financial assistance of Parke, Davis and Company and we wish to express our sincere appreciation for the aid which has been given us.

Voegtlin[2] accounts for the therapeutic activity of salvarsan by the assumption that the latter compound, in the body, is oxidized slowly to the corresponding arsine oxide.

It seemed to us that another substance, a possible percursor of the arsine oxide, might play an important role in the transformation of an arseno compound in the animal body.

If a substance of the arseno type, arsenobenzene for example, undergoes progressive oxidation in the presence of moisture, the first oxidation product may be a compound of structure I—*sym.*-diphenyldihydroxydiarsyl. Upon further oxidation this substance would be converted into phenylarsine oxide.

$$C_6H_5As{=}AsC_6H_5 \longrightarrow \underset{\text{I}}{C_6H_5(OH)As{-}As(OH)C_6H_5} \longrightarrow [2C_6H_5As(OH)_2] \longrightarrow 2C_6H_5As{=}O$$

It seemed to us desirable to prepare a series of dihydroxy compounds of the above type which we have called "arsenicols" because of their structural resemblance to pinacols.

One of the several methods which suggested themselves for the preparation of diphenylarsenicol was the hydrolysis of diphenyldi-iododiarsyl, $C_6H_5(I)As\text{-}As(I)C_6H_5$. We found that this latter substance can be prepared easily but that, when dissolved, it absorbs oxygen with great rapidity. In fact, a solution of this material is just as reactive toward oxygen as solutions of tetra-aryldiarsyls or triarylmethyls.

In view of this property and other unexpected reactions which diphenyldi-iododiarsyl undergoes it seemed not only desirable but necessary to study a series of diaryldi-iododiarsyls before we undertook the synthesis of the corresponding dihydroxyl derivatives.

We have obtained, in addition to the diphenyl compound, the di-*p*-tolyl-, di-*p*-anisyl,- di-α-naphthyl- and dibiphenyldi-iododiarsyl and found that these substances behave essentially in the same manner as the phenyl analog.

Diphenyldi-iododiarsyl was prepared by the action of crystalline phosphorous acid on phenyldi-iodo-arsine, dissolved in alcohol. The diarsyl had been obtained previously by Michaelis and Schulte[3] by this method

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[2] Voegtlin and Smith, *J. Pharmacol.*, 16, 199 (1920); Voegtlin, *Physiol. Reviews*, 5, 79 (1925).

[3] Michaelis and Schulte, *Ber.*, 14, 913 (1881); *ibid.*, 15, 1953 (1882). These investigators also isolated the compound in an impure state from the interaction of phenylarsine oxide, phosphorous and hydriodic acids. Michaelis, *Ann.*, 320, 333, 337 (1902), states that 2,2′,4,4′-tetramethylarsenobenzene and 2,2′,5,5′-tetramethylarsenobenzene react additively with iodine to form the corresponding diaryldi-iododiarsyls but no description of these compounds, other than the analyses and melting points, is given. Steinkopf, Schmidt and Smie, *Ber.*, 59, 1469 (1926), obtained ethylphenyldi-iododiarsyl, $C_2H_5(I)As\text{-}As(I)C_6H_5$, from ethylphenyldiarsylene, $C_2H_5As{=}AsC_6H_5$, and iodine.

and was described as a very unstable substance which decomposes into phenyldi-iodo-arsine and phenylarsonic acid when exposed to the air.

Dissolved in bromobenzene, tetraphenyldiarsyl[4] reacts with oxygen, instantly, in the ratio of one molecular equivalent of the diarsyl to ***one*** molecular equivalent of the gas; under the same conditions diphenyldi-iododiarsyl absorbs oxygen in the proportion of one molecular equivalent of the former to *one-half* of a molecular equivalent of the latter.

$$2(C_6H_5)_2As{-}As(C_6H_5)_2 + 2O_2(+H_2O) \longrightarrow (C_6H_5)_2As{-}O{-}As(C_6H_5)_2 + 2(C_6H_5)_2As(O)OH\text{[5]}$$

$$2C_6H_5(I)As{-}As(I)C_6H_5 + O_2 \longrightarrow 2C_6H_5As{=}O + 2C_6H_5AsI_2 \qquad \text{(A)}$$

The arylarsine oxide and the aryldi-iodo-arsine were isolated, in the case of the phenyl and *p*-tolyl compounds, in good yields with respect to formulation A.

In addition to the difference in the amount of oxygen absorbed, another essential variation in the behavior of tetraphenyldiarsyl and diphenyldi-iododiarsyl is that during the oxidation of the former compound the group $(C_6H_5)_2As{-}$ remains intact while in the case of the latter substance iodine is eliminated from the radical $C_6H_5(I)As{-}$. A red color develops during the oxidation of diphenyldi-iododiarsyl and its analogs but disappears very rapidly; if the solution of the diarsyl is shaken too slowly during the interaction with oxygen, the formation of this color may escape notice. The red color[6] is due, undoubtedly, to the formation of free iodine. The evolution of iodine indicates that formulation A represents the summation of several reactions. Probably the first reaction is one which ensues from diphenyldi-iododiarsyl and oxygen with the formation of a peroxide or dioxide which decomposes spontaneously with the liberation of iodine. The latter reacts rapidly with diphenyldi-iododiarsyl to form phenyldi-iodo-arsine, as we have shown in a separate experiment.

$$C_6H_5(I)As{-}As(I)C_6H_5 + O_2 \longrightarrow \text{peroxide or dioxide} \longrightarrow I_2 \qquad \text{(B)}$$

$$C_6H_5(I)As{-}As(I)C_6H_5 + I_2 \longrightarrow 2C_6H_5AsI_2 \qquad \text{(C)}$$

As soon as phenylarsine oxide is formed (formulation A) this compound, too, reacts instantly with iodine, presumably, to form an unstable com-

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[4] (a) Blicke and Smith, THIS JOURNAL, 51, 2273 (1929); (b) Blicke, Weinkauff and Hargreaves, *ibid.*, 52, 780 (1930).

[5] The initial reaction product may be a peroxide. When the oxidized solution of the tetra-aryldiarsyl is exposed to the moisture in the atmosphere and the solvent then removed, tetraphenylarsyl oxide and diphenylarsinic acid are formed, but so far we have not been able to obtain them in the ratio indicated above.

[6] This phenomenon can be observed best if a saturated ether solution of diphenyl-di-iododiarsyl is placed in a tall open cylinder over a small amount of solid diphenyldi-iododiarsyl. An intense red color soon develops in the upper part of the solution and disappears instantly when the mixture is shaken; in a short time the red color reappears. This process can be repeated as long as any unchanged diphenyldi-iododiarsyl is present. The iodine color finally becomes permanent.

pound of the type $C_6H_5(I_2)As{=}O$. Neither phenylarsine oxide nor phenyldi-iodo-arsine absorbs oxygen.

Since iodine interacts with diphenyldi-iododiarsyl to form phenyldi-iodo-arsine, diphenyldi-iododiarsyl should absorb less oxygen after the addition of iodine. Accordingly, it was found that after the addition of two molecular equivalents of iodine, four molecular equivalents of the diarsyl absorb only one molecular equivalent of the gas.

$$\begin{array}{l} 4C_6H_5(I)As{-}As(I)C_6H_5 + 2I_2 \longrightarrow 2C_6H_5(I)As{-}As(I)C_6H_5 + 4C_6H_5AsI_2 \\ 2C_6H_5(I)As{-}As(I)C_6H_5 + O_2 \longrightarrow 2C_6H_5AsI_2 + 2C_6H_5As{=}O \\ \hline 4C_6H_5(I)As{-}As(I)C_6H_5 + 2I_2 + O_2 \longrightarrow 6C_6H_5AsI_2 + 2C_6H_5As{=}O \qquad \text{(D)} \end{array}$$

Mercury reacts almost instantly with phenyldi-iodo-arsine to form diphenyldi-iododiarsyl; the latter compound also reacts with mercury, but much more slowly, to form arsenobenzene.

$$2C_6H_5AsI_2 + \mathbf{Hg\ (excess)} \longrightarrow C_6H_5(I)As{-}As(I)C_6H_5 \qquad \text{(E)}$$

$$C_6H_5(I)As{-}As(I)C_6H_5 + \mathbf{Hg\ (excess)} \longrightarrow C_6H_5As{=}AsC_6H_5 \qquad \text{(F)}$$

It was stated previously that diphenyldi-iododiarsyl absorbs one-half of a molecular equivalent of oxygen; however, if mercury is added to a solution of diphenyldi-iododiarsyl and the latter then allowed to react with oxygen immediately after addition of the metal, ***one*** molecular equivalent of the gas is absorbed for each molecular equivalent of the diarsyl. Phenylarsine oxide is the only reaction product formed and this substance was isolated in practically quantitative yield.

$$2C_6H_5(I)As{-}As(I)C_6H_5 + \mathbf{Hg\ (excess)} + 2O_2 \longrightarrow 4C_6H_5As{=}O \qquad \text{(G)}$$

In this instance the diarsyl reacts first with oxygen according to formulation A and the phenyldi-iodo-arsine produced is then converted rapidly by mercury into diphenyldi-iododiarsyl (formulation E). Reactions A and E continue, alternately, until all of the diarsyl is oxidized to phenylarsine oxide. The mercury also reacts with the iodine, as fast as it is liberated, and thus prevents the formation of phenyldi-iodo-arsine from diphenyldi-iododiarsyl and iodine (formulations B and C).

Since it was found that phenyldi-iodo-arsine and arsenobenzene react almost instantly at ordinary temperature to form diphenyldi-iododiarsyl, phenyldi-iodo-arsine and arsenobenzene mixed in accordance with the ratio

$$C_6H_5AsI_2 + {}^1/{}_2C_6H_5As{=}AsC_6H_5 \longrightarrow C_6H_5(I)As{-}As(I)C_6H_5 \qquad \text{(H)}$$

shown in formulation H should absorb rapidly one-half of a molecular equivalent of oxygen (formulation A). This was found to be the case.

Arsenobenzene, suspended in bromobenzene, does not absorb oxygen. However, if iodine is added to the solution the latter absorbs the gas with great rapidity; furthermore, the amount of the gas which enters into the reaction depends upon the quantity of iodine added. For example, when four molecular equivalents of iodine were used the solution absorbed, very rapidly, two molecular equivalents of oxygen (formulation I) but

$$4C_6H_5As{=}AsC_6H_5 + 4I_2 \longrightarrow 4C_6H_5(I)As{-}As(I)C_6H_5$$
$$4C_6H_5(I)As{-}As(I)C_6H_5 + 2O_2 \longrightarrow 2C_6H_5As{=}O + 2C_6H_5AsI_2$$
$$\overline{4C_6H_5As{=}AsC_6H_5 + 4I_2 + 2O_2 \longrightarrow 4C_6H_5As{=}O + 4C_6H_5AsI_2} \qquad (I)$$

when only two molecular equivalent of the halogen were used the solution absorbed three molecular equivalents of the gas (formulation J). If only

$$4C_6H_5As{=}AsC_6H_5 + 2I_2 \longrightarrow 2C_6H_5(I)As{-}As(I)C_6H_5 + 2C_6H_5As{=}AsC_6H_5$$
$$2C_6H_5(I)As{-}As(I)C_6H_5 + O_2 \longrightarrow 2C_6H_5As{=}O + 2C_6H_5AsI_2$$
$$2C_6H_5As{=}AsC_6H_5 + 2C_6H_5AsI_2 \longrightarrow 2C_6H_5(I)As{-}As(I)C_6H_5 + C_6H_5As{=}AsC_6H_5$$
$$2C_6H_5(I)As{-}As(I)C_6H_5 + O_2 \longrightarrow 2C_6H_5As{=}O + 2C_6H_5AsI_2$$
$$C_6H_5As{=}AsC_6H_5 + 2C_6H_5AsI_2 \longrightarrow 2C_6H_5(I)As{-}As(I)C_6H_5$$
$$2C_6H_5(I)As{-}As(I)C_6H_5 + O_2 \longrightarrow 2C_6H_5As{=}O + 2C_6H_5AsI_2$$
$$\overline{4C_6H_5As{=}AsC_6H_5 + 2I_2 + 3O_2 \longrightarrow 6C_6H_5As{=}O + 2C_6H_5AsI_2} \qquad (J)$$

a trace of iodine or phenyldi-iodo-arsine is added to the solution of arsenobenzene, the latter in each case should react with four molecular equivalents of oxygen in accordance with formulations K and L. In these

$$4C_6H_5As{=}AsC_6H_5 + I_2 \text{ (trace)} + 4O_2 \longrightarrow 8C_6H_5As{=}O + C_6H_5AsI_2 \text{ (trace)} \qquad (K)$$
$$4C_6H_5As{=}AsC_6H_5 + C_6H_5AsI_2 \text{ (trace)} + 4O_2 \longrightarrow 8C_6H_5As{=}O + C_6H_5AsI_2 \text{ (trace)} \qquad (L)$$

instances we found, however, that the amount of oxygen absorbed was in excess of four molecular equivalents—in the case of iodine the absorption was between five and six molecular equivalents and when phenyldi-iodo-arsine was used the solution absorbed between four and five equivalents of the gas. We have no explanation, at present, for this apparent anomalous behavior.

If phenyldi-iodo-arsine, arsenobenzene and iodine are mixed in the ratio expressed in formulation M, the mixture does not absorb oxygen because

$$2C_6H_5AsI_2 + C_6H_5As{=}AsC_6H_5 + 2I_2 \longrightarrow 4C_6H_5AsI_2 \qquad (M)$$

of the quantitative formation of phenyldi-iodo-arsine; but if one-half of the amount of iodine, employed in reaction M, is used the mixture absorbs one-half of a molecular equivalent of oxygen for each two molecular equivalents of diphenyldi-iodo-arsine.

$$2C_6H_5AsI_2 + C_6H_5As{=}AsC_6H_5 + I_2 \longrightarrow 2C_6H_5AsI_2 + C_6H_5(I)As{-}As(I)C_6H_5$$
$$C_6H_5(I)As{-}As(I)C_6H_5 + {}^1/_2O_2 \longrightarrow C_6H_5As{=}O + C_6H_5AsI_2$$
$$\overline{2C_6H_5AsI_2 + C_6H_5As{=}AsC_6H_5 + I_2 + {}^1/_2O_2 \longrightarrow 3C_6H_5AsI_2 + C_6H_5As{=}O} \qquad (N)$$

Diphenyldibromodiarsyl was prepared from phenyldibromo-arsine and arsenobenzene. This compound, after isolation, proved to be just as reactive toward oxygen as the corresponding iodo derivative. However, the amount of oxygen absorbed by diphenyldibromodiarsyl is greater than that absorbed by an equivalent quantity of diphenyldi-iododiarsyl and is less than that required for the oxidation of tetraphenyldiarsyl.

Several unsuccessful attempts were made to obtain diphenyldichlorodiarsyl from phenyldichloro-arsine and arsenobenzene.

A series of molecular weight determinations of various diaryldihalodiarsyls proved that in the event that any of these compounds dissociated into divalent arsenic radicals the degree of dissociation is too low to be established by the molecular weight method.

Experimental Part

Aryldi-iodo-arsines.—The arylarsine oxides were heated on a steam-bath for two hours with approximately ten times the calculated amount of hydriodic acid (sp. gr. 1.7). The iodides, which precipitated either as oils or solids, were separated, washed with water and dried in a vacuum desiccator over soda lime. Although aryldi-iodo-arsines can be obtained from aryldichloro-arsines and sodium iodide in acetone[7] solution, this method, in the case of phenyldi-iodo-arsine, yielded an oily iodide which rapidly turned deep red and gradually deposited a considerable amount of solid material. The phenyl,[8] tolyl[9] and anisyl[10] derivatives are oils. The a-naphthyl and the biphenyl compounds, which had not been prepared hitherto, are yellow solids which crystallize readily from benzene.

TABLE I

ARYLDI-IODO-ARSINES

Compound	M. p., °C.	Formula	Iodine analyses[a] Calcd.	Found
α-Naphthyl	106–108	$C_{10}H_7AsI_2$	55.70	55.56
Biphenyl	104–106	$C_{12}H_9AsI_2$	52.69	52.47

[a] Thompson and Oakdale method, THIS JOURNAL, 52,1195 (1930).

Diaryldi-iododiarsyls.—These compounds can be prepared according to the following general methods illustrated in the case of phenyldi-iododiarsyl: (a) six g. of phenyldi-iodo-arsine, suspended in 25 cc. of absolute alcohol, and 10 g. of crystalline phosphorous acid, dissolved in 125 cc. of absolute alcohol, were introduced separately into a free radical apparatus[11] of 250 cc. capacity and the latter rotated for twelve hours on a shaking machine. The diarsyl separated in a finely divided, deep yellow, crystalline form. The supernatant alcoholic layer was removed through the side arm of the apparatus with the aid of suction and the product washed four times with anhydrous ether which had been saturated with nitrogen. In order to dry the compound the apparatus was allowed to remain attached to a suction pump for five hours; to avoid decomposition the material should not be heated during this process. The diarsyl was isolated in the manner described previously in the case of tetra-aryldiarsyls.[4b]

(b) Phenylarsine oxide, suspended in 25 cc. of absolute alcohol, was put into a free radical apparatus. Ten cc. of hydriodic acid (sp. gr. 1.7) and 10 g. of phosphorous acid, dissolved in 125 cc. of absolute alcohol, were then added. The oxide dissolves immediately and after a short time the diarsyl begins to precipitate.

(c) Arsenobenzene, suspended in alcohol, was put into a radical apparatus and treated with phenyldi-iodo-arsine, suspended in the same solvent. The compounds were used in the ratio of one mole of the arseno compound to two and one-half moles of the di-iodide. The mixture was rotated for twelve hours.

(d) One and one-half grams of arsenobenzene, suspended in 25 cc. of benzene which had been saturated with nitrogen, was treated slowly in a radical apparatus with 1.3 g. of iodine dissolved in benzene. The mixture was rotated for three hours.

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[7] Steinkopf and Schwen, *Ber.*, 54, 1463 (1921).

[8] Michaelis and Schulte, *ibid.*. 14, 913 (1881); Burrows and Turner, *J. Chem. Soc.*, 117, 1376 (1920); Steinkopf and Schwen, *Ber.*, 54, 1463 (1921).

[9] LaCoste and Michaelis, ibid., 11, 1889 (1878); Ann., 201, 248 (1880).

[10] Michaelis, *ibid.*, 320, 301 (1902). Bertheim, *Ber.*, 47, 276 (1914).

[11] Gomberg and Cone, *ibid.*, 37,2034 (1904). The lower stopcock was eliminated.

The benzene layer was decanted from the solid material which had separated and the latter was washed with ether.

(e) Six grams of phenyldi-iodo-arsine, dissolved in 100 cc. of oxygen-free bromobenzene, was shaken with 10 g. of mercury for fifteen minutes in a tightly stoppered bottle. The mixture was warmed in a bath, without exposure to air, in order to dissolve the diarsyl which had separated, and then filtered into a radical apparatus. The latter was immersed in a bath heated to 80° and about 75 cc. of the solvent was removed under diminished pressure. Ether was then added to precipitate the diarsyl, the solvent removed by decantation and the solid material washed with ether.

Diphenyldibromodiarsyl.—One and one-half grams (0.005 mole) of arsenobenzene and 5.0 g. (0.008 mole) of phenyldibromo-arsine were washed into a free radical apparatus of 100-cc. capacity with the aid of ether. The side arm of the apparatus was connected with a suction pump and after the ether had been removed under diminished pressure the bulb of the apparatus was heated in a glycerol-bath to 135° until a clear yellow liquid was obtained. The diarsyl, which separated in crystalline form when the mixture was cooled, was washed five times with oxygen-free ether in order to remove all excess phenyldibromo-arsine. In order to dry the material, the bulb of the apparatus was evacuated continuously, at ordinary temperature, for five hours. The compound was removed from the apparatus in the manner described previously. Diphenyldibromodiarsyl is a light yellow, crystalline substance which melts, in a tube filled with nitrogen, at 122–124°. Dissolved in bromobenzene, 1.099 g. of the material absorbed 38 cc. of oxygen, under standard conditions of temperature and pressure, in less than thirty seconds.

Anal. Calcd. for $C_{12}H_{10}As_2Br_2$: Br, 34.48. Found: Br, 35.05.

TABLE II

DIARYLDI-IODODIARSYLS

Diarsyl[a,b]	M. p., °C.[c]	Oxygen absorp., (N. T. P.) Cc.	Sample, g.	% Absorp.[d]	Iodine analyses[e] Formula	Calcd.	Found
Diphenyl	176–177[f]	33	1.569	103	$C_{12}H_{10}As_2I_2$	45.58	45.52
Di-*p*-tolyl	149–150	31	1.567	105	$C_{14}H_{14}As_2I_2$	43.34	42.87
Di-p-anisyl	135–137	18	0.981	103	$C_{14}H_{14}O_2As_2I_2$	41.10	40 54
Di-a-naphthyl	176–178	18	1.068	105	$C_{20}H_{14}As_2I_2$	38.60	34.35'
Dibiphenyl	244–246[h]	38	2.304	105	$C_{24}H_{18}As_2I_2$	35.77	32 50[g]

[a] All of these compounds were prepared according to Method (a). In the case of the naphthyl and biphenyl diarsyls the di-iodide was dissolved in the least amount of warm benzene instead of alcohol. [b] The diarsyls listed above are all deep yellow, well-defined crystalline compounds and are insoluble in alcohol. The phenyl compound is slightly soluble in hot benzene and hot chloroform while the tolyl and naphthyl derivatives are quite soluble in these solvents. [c] All melting points were determined in sealed tubes filled with nitrogen. The compounds softened somewhat at temperatures below the melting points, gradually changed in color from yellow to red and melted with the formation of a deep red liquid. [d] Calculated on the basis of formulation A. "Thompson and Oakdale method, THIS JOURNAL, 52, 1195 (1930). [f] Michaelis and Schulte [*Ber.*, 14, 913 (1881); *ibid.*, 15, 1954 (1882)] recorded no melting point for this substance. [g] A number of iodine analyses were made in the case of the naphthyl and biphenyl compounds but the results obtained were invariably low. Although the material had always been dried to constant weight before analysis, the latter may still have been contaminated by a small amount of solvent or, possibly, by a small quantity of the corresponding arseno compound. [h] Melts with decomposition.

Attempt to Prepare **Diphenyldichlorodiarsyl.**—There is no apparent reaction between phenyldichloro-arsine and arsenobenzene when the compounds are mixed at ordinary temperature. However, the mixture absorbs oxygen, as is shown by the following experiment.

Six hundred and eight thousandths of a gram (0.002 mole) of arsenobenzene, suspended in 25 cc. of oxygen-free bromobenzene, was put into an absorption bottle. Eight hundred and ninety thousandths of a gram (0.004 mole) of phenyldichloro-arsine was placed in a thin-walled test-tube and the latter introduced into the absorption bottle. When the test-tube was broken and the components were allowed to mix, oxygen was absorbed immediately. The suspended arsenobenzene gradually dissolved and, after the mixture had been agitated continuously for twenty minutes on a shaking machine, a clear, colorless solution was obtained. Seventy cc. (N. T. P.) or 0.003 mole of the gas was absorbed.

When arsenobenzene and excess phenyldichloro-arsine were heated, the former substance dissolved. A crystalline precipitate was obtained when the mixture was cooled but from the latter we were able to isolate only arsenobenzene.

Oxidation Products of Diphenyl- and **Di-p-tolyldi-iododiarsyl.**—Ten grams of solid diphenyldi-iododiarsyl was exposed to the air for twelve hours. The semi-liquid mass was extracted with a mixture of equal parts of ether and petroleum ether (40–60°)

TABLE III

OXYGEN ABSORPTIONS[a]

	Phenyl-dihalo-arsine moles	Arsenobenzene, mole	Hg, cc.	Iodine, mole	Absorp. found, cc. (N. T. P.)	Absorp. calcd. according to equation, cc.
1	0.004 (I)	..	1[b]	...	48	45 (E)
2	.004 (I)	..	1[c]	...	0	0 (E-F)
3	.004 (I)	0.002		...	44	45 (H)
4	....	.005	.	0.0050	62	56 (I)
5	....	.005	.	0.0025	88	84 (J)
6	....	.002		Trace	62	45 (K)
7	....	.002		Trace	62	45 (K)
8	1 drop (I)	.002		...	58	45 (L)
9	0.004 (Br)[d]	.002		...	75	..
10	.004 (Cl)	.002		...	70	..
11	.004	.002		.004	0	0 (M)
12	.004	.002		.002	22	22 (N)

1.377 g. of diphenyldi-iododiarsyl and 1 cc. of Hg (F) absorbed 63 cc. after the mixture had been shaken for several minutes in the presence of oxygen; calcd. 56 cc.

[a] In the first nine experiments listed, as well as in Expt. 12, the volume of oxygen recorded was absorbed in less than two minutes. In Expt. 10 the absorption was slower, hence the volume recorded in this experiment was that obtained after one-half hour's contact with the gas. [b] The mixture was shaken for ten minutes prior to absorption. [c] The mixture of phenyldi-iodo-arsine and mercury was shaken in a sealed tube for twenty-four hours prior to the absorption. [d] Four thousandths of a mole of phenyldibromo-arsine and two thousandths of a mole of arsenobenzene yield, according to the following equation, four thousandths of a mole of diphenyldibromodiarsyl. This

$$2C_6H_5AsBr_2 + C_6H_5As{=}AsC_6H_5 \longrightarrow 2C_6H_5(Br)As{-}As(Br)C_6H_5$$

mixture absorbed 75 cc. (N. T. P.) of oxygen. It was found that 1.17 g. (0.0025 mole) of isolated diphenyldibromodiarsyl absorbed 48 cc. (N. T. P.) of oxygen. If exactly four thousandths of a mole of the diarsyl had been used, the absorption would have been 75 cc.

TABLE IV

MOLECULAR WEIGHT DETERMINATIONS[a,b]

	R(X)As—As(X)R R	X	Solvent	At, °C.	Mol. wt. found	Mol. wt. calcd.
1	Phenyl	I	Benzene	0 3129	527	558
2	Phenyl	I	Chloroform	.1155	559	558
3	Phenyl	I	Biphenyl	.538	528	558
4	*p*-Tolyl	I	Benzene	.1887	570	586
5	*p*-Tolyl (oxidized)	I	Benzene	.1023	290	293[c]
6	α-Naphthyl	I	Benzene	.1056	610	658
7	Phenyl	Br	Benzene	.2739	430	464

[a] A considerable number of molecular weight determinations have been made but in order to conserve space we have recorded only the values obtained with the highest concentrations, approximately 3%, of the diarsyl solutions. In several series of duplicate determinations with the same diarsyl, low molecular weight values would be obtained occasionally in one series of experiments. These low values were due, undoubtedly, to the presence of traces of oxygen in the molecular weight apparatus at the time the first pellet of the diarsyl was introduced. The decomposition by oxygen of a diaryldi-iododiarsyl into an arylarsine oxide and an aryldi-iodo-arsene would tend to lower the molecular weight value and after complete oxidation the molecular weight found should be approximately one-half that calculated for the diaryldi-iododiarsyl. In the case of di-p-tolyldi-iododiarsyl a stream of oxygen was passed through a benzene solution of the material after the molecular weight had been determined. Prior to oxidation (Expt. 4) the molecular weight was found to be 570; after oxidation the value 290 (Expt. 5) was obtained. In Expt. 3 the cryoscopic method was used; all other determinations were made by the ebullioscopic procedure with the use of the Menzies apparatus. All solvents used had been saturated with dry, oxygen-free nitrogen and the molecular weight apparatus was filled with nitrogen prior to a determination. A stream of nitrogen passed through the top of the apparatus prevented the entrance of oxygen. Because of the insolubility of dibiphenyldi-iododiarsyl the molecular weight of this substance was not determined. [b] The purity of each diarsyl was established by analysis, oxygen absorption and melting point prior to the molecular weight determination. [c] Approximate value.

in order to remove phenyldi-iodo-arsine. There were obtained 2.45 g. of phenylarsine oxide, m. p. 138–140°, and 7.8 g. of phenyldi-iodo-arsine. The calculated amount (formulation A) of the former substance is 3.0 g. and that of the latter is 7.4 g. In order to identify phenyldi-iodo-arsine it was hydrolyzed with alkali to phenylarsine oxide.

From 1.5 g. of di-p-tolyldi-iododiarsyl there was obtained 0.4 g. of tolylarsine oxide, m. p. 179–182°, and 1.1 g. of tolyldi-iodo-arsine. The latter substance was identified by conversion into the corresponding arsine oxide.

Action of Mercury on Phenyldi-iodo-arsine and Diphenyldi-iododiarsyl.—Six grams of phenyldi-iodo-arsine, dissolved in 125 cc. of oxygen-free benzene, was shaken for three days with 3 cc. of mercury in a tightly stoppered bottle. The reaction mixture was filtered and the residue washed thoroughly with benzene. From the benzene filtrate a very small quantity of triphenylarsine was isolated in the form of the mercuric chloride addition product.[12] The residue was moistened with alcohol and then treated with an aqueous solution of potassium iodide in order to remove mercury salts. Arsenobenzene was obtained and identified by a mixed melting point. The yield was 2.1 g. or 95% of the calculated amount.

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[12] A much larger amount of the triphenylarsine mercuric chloride addition product was obtained when arsenobenzene was shaken with mercury and mercuric iodide.

When diphenyldi-iododiarsyl was treated in the manner described above, arsenobenzene was obtained as a reaction product.

Summary

Diphenyl-, di-*p*-tolyl-, di-panisyl-, di-a-naphthyl- and dibiphenyldi-iododiarsyl as well as diphenyldibromodiarsyl have been prepared. Each of the above-mentioned di-iododiarsyls, in solution, absorbs oxygen with great rapidity but the amount of gas absorbed is only one-half of that required for the oxidation of an equivalent amount of a tetra-aryldiarsyl. The molecular quantity of oxygen absorbed by diphenyldibromodiarsyl is intermediate between the amount required for the oxidation of a diaryldi-iododiarsyl and a tetra-aryldiarsyl.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

THE PROPERTIES AND MOLECULAR STATE OF CERTAIN ORGANIC ARSENICALS

BY F. F. BLICKE AND F. D. SMITH[1]

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During our investigations of diarsyls it became necessary to prepare a variety of simple aromatic arsenicals. Inasmuch as the properties of some of the compounds had not been determined very extensively, we studied a number of them more in detail. It was found that arsenobenzene and certain of its analogs, contrary to most of the statements in the literature, are colorless, stable compounds which undergo no decomposition when exposed to the atmosphere or to pure oxygen under ordinary conditions. Maschmann[2] claims that arsenobenzene reacts explosively with oxygen at ordinary temperature and Palmer and Scott,[3] although they obtained arsenobenzene in a colorless state,[4] took great precautions in the isolation of the material to prevent oxidation.

We found, however, that if traces of certain substances are added to a solution of arsenobenzene the latter begins, instantly, to absorb oxygen and in a comparatively short time has reacted with an amount of the gas which corresponds, in some instances at least, to the quantity of oxygen required for the formation of phenylarsine oxide. Substances discovered so far which induce the absorption of oxygen by arsenobenzene are hydrochloric, hydrobromic, hydriodic, sulfuric and nitric acids, iodine, diphenylbromo-arsine, diphenyliodo-arsine, phenyldichloro-arsine, phenyldibromo-arsine, phenyldi-iodo-arsine and triphenylbromomethane.

[1] Parke, Davis and Company Research Assistant, 1929–1930.

[2] Maschmann, *Ber.*, 59, 1143 (1926).

[3] Palmer and Scott, THIS JOURNAL, 50, 537 (1928).

[4] Steinkopf and Dudek [*Ber.*, 62, 2494 (1929)] reported that arsenobenzene is colorless.

The fact that other investigators have reported unsubstituted aromatic arseno compounds[5] to be unstable toward oxygen is due, undoubtedly, to the circumstance that the arseno compounds obtained by them were contaminated by traces of impurities. The statements that their arseno compounds were colored and the fact that they melted at temperatures much lower than those found by us also lead one to this conclusion. Impurities may have been introduced as the result of either insufficient or too complete reduction of the arylarsonic acid or the arylarsine oxide from which the arseno compounds were obtained. In the former case there may have been produced small amounts of a diaryldihydroxydiarsyl, R(OH)As-As(OH)R, a type of compound which will be discussed in a later paper; in the latter instance a small quantity of a diaryldiarsyl R(H)AsAs(H)R, or an arylarsine, $RAsH_2$, may have been formed. Furthermore, it is possible that the arseno compounds may have been contaminated with traces of such substances as have been listed above.

Phenylarsine oxide, phenylarsine sulfide, phenylarsine imide, arsenobenzene and a number of aromatic analogs of these compounds exist, when dissolved, in an associated state and the degree of association is dependent upon the solvent in which the compound is dissolved.[6]

Certain regularities have been observed as far as the substances which we have investigated are concerned. Thus compounds in which the arsenic atom is linked by a single bond to another atom except arsenic[7] are stable toward oxygen and yield normal molecular weight values; these compounds have been placed in Group I. Compounds which contain an arsenic atom attached to arsenic or some other atom by a double bond do not react with oxygen under ordinary conditions and exist, in solution, in an associated state; these have been placed in Group II. Finally, arsenicals in which an arsenic atom is attached directly to another arsenic atom by a single bond react instantly with oxygen under ordinary conditions. Based on molecular weight determinations and chemical behavior there is some indication that such compounds may dissociate into divalent arsenic radicals, although the experimental results obtained so far are not conclusive.[8] Substances of the latter type represent Group III.[9]

Group I—Normal molecular weight, stable toward oxygen.

Group 11—Abnormal molecular weight (association), stable toward oxygen.

Group 111—Molecular weights somewhat abnormal (dissociation ?), react with oxygen instantly.

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[5] The behavior of substituted aromatic arseno compounds is being investigated.

[6] Undoubtedly temperature is another factor which affects the degree of association.

[7] It is possible that compounds which contain arsenic attached to phosphorus, nitrogen, antimony or bismuth would behave in a similar manner.

[8] Blicke, Weinkauff and Hargreaves, THIS JOURNAL, 52, 780 (1930).

[9] Whether or not all aromatic arsenicals can be grouped in accordance with the above scheme can only be determined by a more extensive investigation.

GROUP I

$(C_6H_5)_2AsI$
$C_6H_5AsCl_2$ $(C_6H_5)_3As$
$(C_6H_5)_2As—O—As(C_6H_5)_2$
$(p\text{-}CH_3C_6H_4)_2As—O—As(C_6H_5CH_3\text{-}p)_2$
$(\alpha\text{-}C_{10}H_7)_2As—O—As(C_{10}H_7—\alpha)_2$
$(C_6H_5)_2As—S—As(C_6H_5)_2$

GROUP II

$(C_6H_5As{=}O)_x$ $(p—CH_3C_6H_4As{=}O)_x$
$(p\text{-}CH_3OC_6H_4As{=}O)_x$
$(C_6H_5As{=}S)_x$ $(C_6H_5As{=}NH)_x$
$(C_6H_5As{=}AsC_6H_5)_x$
$(p\text{-}CH_3C_6H_4As{=}AsC_6H_4CH_3\text{-}p)_x$
$(p\text{-}CH_3OC_6H_4As{=}AsC_6H_4OCH_3\text{-}p)_x$

GROUP III

$R_2As—AsR_2$[a] $R(I)As—As(I)R$[b]

[a] The properties and molecular weights of a series of aromatic compounds of this type are discussed by Blicke and Smith, THIS JOURNAL, **51,** 2272 (1929), and by Blicke, Weinkauff and Hargreaves, *ibid.*, **52,** 780 (1930). Compounds of this type will be described in our next publication.

Experimental Part

Arylarsine Oxides.—All of the oxides with the exception of phenylarsine oxide were prepared as outlined previously.[10] In order to obtain phenylarsine oxide one part of phenylarsonic acid,[11] dissolved in two parts of concd. hydrochloric acid, was reduced to phenyldichloro-arsine with sulfur dioxide and a trace of potassium iodide. The dichloro compound was purified by distillation under diminished pressure. It was then added, drop by drop, with vigorous stirring to an excess of aqueous alkali. The alkaline solution of phenylarsine oxide was filtered and the oxide precipitated by the addition of ammonium chloride. The crude, dry oxide was dissolved in chloroform and precipitated by the addition of ether; m. p. 142–144".

Phenylarsine Sulfide.—This substance was prepared from phenyldichloro-arsine and hydrogen sulfide in alcoholic solution.[12] The sulfide, which separated as an oil, was dissolved in hot benzene, filtered, cooled and precipitated with alcohol. After recrystallization from bromobenzene the compound melted at 174–176". Schulte recorded the melting point at 152°.

Anal. Calcd. for C_6H_5AsS: S, 17.42. Found: S, 17.60.

For the analysis of sulfur compounds we used a modification of the procedure developed by Wolesensky[13] for the determination of sulfur in rubber.[14] The sample, 0.5–1.0 g., is treated, cautiously, with 10 cc. of concd. nitric acid (sp. gr. 1.42) in a 300-cc. Kjeldahl flask. After the initial reaction has subsided the mixture is boiled until the organic matter is charred completely. Twenty cc. of 70% perchloric acid is added and the mixture heated until a clear, colorless solution is obtained. The nitric acid is then removed completely by boiling the mixture; the latter should be heated until fumes of perchloric acid become pronounced. The solution is transferred to a 800-cc. beaker and diluted to 400 cc. After neutralization with sodium hydroxide and the addition of 5 cc. of concd. hydrochloric acid, *N*/4 barium chloride solution is added slowly to the hot solution until precipitation is complete. The mixture is heated for an hour on a hot-plate, filtered, the precipitate washed with hot water and ignited.

Arsenic and sulfur can be determined in the same sample, provided the latter does not contain bromine or iodine, in the following manner: after decomposition of the organic matter and the removal of the nitric acid as described above, 10 g. of hydrazine

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[10] Blicke and Smith, THIS JOURNAL, **51,** 3480 (1929).

[11] Bart, *Ann.*, 429, 76 (1929).

[12] Schulte, *Ber.*, **15,** 1953 (1882).

[13] Wolesensky, *Ind. Eng. Chem.*, **20,** 1234 (1928).

[14] We wish to express our indebtedness to Mr. J. J. Thompson and Mr. U. O Oakdale for their assistance in this part of the investigation.

hydrochloride, 110 cc. of concd. hydrochloric acid and 1 g. of potassium bromide are added. The arsenic trichloride is then distilled[15] and titrated with *N*/10 potassium bromate; methyl orange is used as indicator.

The residue is treated with nitric acid to destroy the excess hydrazine hydrochloride and boiled until fumes of perchloric acid appear. The subsequent procedure for the determination of sulfur is the same as described above.

If the sample contains only arsenic the following process can be used. After decomposition of the organic matter and removal of the nitric acid the perchloric acid solution is diluted to 100 cc. The solution is then treated with sulfur dioxide in order to reduce the arsenic to the trivalent state. Excess sulfur dioxide is expelled by heat. The mixture is cooled to 60°, 25 cc. of hydrochloric acid is added and the arsenite is titrated with *N*/10 potassium bromate with methyl orange as indicator.

Arseno Compounds.—The following method was found most convenient for the preparation of these substances. The aryldichloro-arsines were dissolved in hot acetone and treated with approximately five times the calculated amount of a 50% solution of hypophosphorous acid. The arseno compounds crystallized from the hot solution. They were filtered, washed with acetone and recrystallized from bromobenzene. No colored by-products were obtained.

TABLE I

ARSENO COMPOUNDS

R As—As R	M. p., °C.	Formula	Arsenic analyses[a]	
			Calcd.	Found
Phenyl,[b] colorless	212–213	$C_{12}H_{10}As_2$	49.34	49.34
p-Tolyl,[c] colorless	218–219	$C_{14}H_{14}As_2$	45.18	45.11
p-Anisyl,[d] colorless	230–232	$C_{14}H_{14}As_2O_2$	41.20	41.15

[a] The method of Thompson and Oakdale described above was used in the determination of arsenic. [b] Other melting points which have been recorded are 195" [Palmer and Scott, THIS JOURNAL, 50, 539 (1928)], 196° [Michaelis and Schulte, *Ber.*, 14, 912 (1881)], 208° [Binz, Bauer and Hallstein, *ibid.*, 53, 427 (1920)], and 212° [Michaelis and Schäfer, *ibid.*, 46, 1742 (1913)]. [c] Michaelis [*Ann.*, 320, 301 (1902)] stated the melting point to be 184". [d] Michaelis [ibid., 320, 299 (1902)] described this substance as a yellow compound which decomposed at 200°.

TABLE II

ABSORPTION OF OXYGEN BY ARSENOBENZENE IN THE PRESENCE OF CERTAIN COMPOUNDS

Arsenobenzene dissolved in 20 cc. of bromobenzene,[a] g.	Substance added		Cc. of oxygen absorbed after given time (N. T. P.)	Cc. of oxygen required for phenylarsine oxide
0.608	HCl	5 Drops	50 (30 min.)	44.8
.608	HBr	5 Drops	44 (15 min.)	44.8
.608	HI	2 Drops	70 (15 min.)	44.8
.608		2 Drops	26 (30 min.)	44.8
.608	H_2SO_4	2 Drops	45 (60 min.)	44.8
.608	HNO_3	2 Drops	87 (5 min.)	44.8
.608	I	Trace	62 (5 min.)	44.8
.608	$C_6H_5AsI_2$	1 Drop	58 (5 min.)	44.8

[a] Bromobenzene was chosen as a solvent because of its low vapor pressure. The absorption apparatus used was that designed by Gomberg and Schoepfle, THIS JOURNAL. 39, 1661 (1917).

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[15] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, 1927, Vol. I, p. 39b.

Hitherto, aromatic arseno compounds have been obtained by reduction of an arylarsonic acid or an arylarsine oxide, in alcoholic solution, with phosphorous or hypophosphorous acid.

TABLE III
MOLECULAR WEIGHT DETERMINATIONS

Compound	Solvent[a,b]	At, °C.[c]	Mol. wt. found, *A*	Mol. wt. calcd., *B*	*A/B*
$(C_6H_5)_2AsI$	Camphor	11.3	354	356	0.99
$C_6H_5AsCl_2$	Benzene	0.1968	234	223	1.05
$(C_6H_5)_3As$	Camphor	22.5	313	306	1.02
$(C_6H_5)_4As_2O$	Benzene	0.1658	472	474	0.99
$(\alpha\text{-}C_{10}H_7)_4As_2O$	Naphthalene	.059	683	674	1.01
$(C_6H_5)_4As_2S$	Camphor	8.0	499	490	1.02
$C_6H_5As{=}O$	Biphenyl[d]	0.133	664	168	3.94
$C_6H_5As{=}O$	Carbon tetrachloride[e]	.0686	672	168	4.00
$C_6H_5As{=}O$	Benzene	.0955	663	168	3.94
$C_6H_5As{=}O$	Camphor	17.5	672	168	4.00
$p\text{-}CH_3C_6H_4As{=}O$	Benzene	0.0948	716	182	3.93
$p\text{-}CH_3C_6H_4As{=}O$	Chloroform	.120	554	182	3.04
$p\text{-}CH_3C_6H_4As{=}O$	Camphor	16.2	727	182	3.99
$p\text{-}CH_3OC_6H_4As{=}O$	Benzene	0.0869	768	198	3.88
$p\text{-}CH_3OC_6H_4As{=}O$	Chloroform	.1626	395	198	1.99
$p\text{-}CH_3OC_6H_4As{=}O$	Camphor	15.0	785	198	3.97
$C_6H_5As{=}S$	Biphenyl	0.240	738	184	4.01
$C_6H_5As{=}S$	Carbon tetrachloride	.0152	743	184	4.04
$C_6H_5As{=}S$	Camphor	20.0	740	184	4.02
$C_6H_5As{=}NH$[f]	Benzene	...	642	167	3.84
$C_6H_5As{=}AsC_6H_5$[g]	Benzene	0.0205	895	304	2.94
$C_6H_5As{=}AsC_6H_5$[g]	Benzene	.0216	915	304	3.01
$p\text{-}CH_3C_6H_4As{=}AsC_6H_4CH_3$	Chloroform	.0241	810	332	2.44
$p\text{-}CH_3C_6H_4As{=}AsC_6H_4CH_3$	Chloroform	.0444	832	332	2.54
$p\text{-}CH_3OC_6H_4As{=}C_6H_4OCH_3$	Chloroform	.0271	1080	364	2.97
$p\text{-}CH_3OC_6H_4As{=}C_6H_4OCH_3$	Chloroform	.0434	1270	364	3.49

[a] The constant for each solvent was determined by the use of benzophenone.

[b] The Rast method, *Ber.*, 55, 1051 (1922). was employed whenever camphor was used as a solvent. Molecular weights were determined in benzene, chloroform and carbon tetrachloride by the ebullioscopic procedure in the Menzies apparatus, THIS JOURNAL, 43, 2309, 2314 (1921). The cryoscopic method was used in the case of naphthalene and biphenyl.

[c] In many instances, because of the limited solubility of the compounds in the solvents employed, higher values for At than those recorded could not be obtained.

[d] Purification of biphenyl, Chipman and Peltier, Ind. Eng. Chem., 21, 1106 (1929).

[e] The constant for carbon tetrachloride is given by Menzies and Wright, THIS JOURNAL, 43, 2320 (1921), as 32.4. By the use of benzophenone, we determined the constant to be 34. This latter value was used in our calculations.

[f] The molecular weight of this compound has been determined very recently by Ipatiew, Rasuwajew and Stromski, Ber., 62, 604 (1929). The cryoscopic method was used with benzene as a solvent. The molecular weight value given in the above table is that obtained by these investigators.

[g] Michaelis and Schulte, *ibid.*, 46, 1742 (1913), determined the molecular weight of arsenobenzene in benzene by the ebullioscopic method. They obtained the value 399. Palmer and Scott, THIS JOURNAL, 50, 539 (1928), with naphthalene as a solvent found the molecular weight to be 642; in benzene, by the ebullioscopic method, 402 and in carbon disulfide 334.

Summary

The properties and molecular weight determinations of a number of simple aromatic arsenic compounds have been recorded. Some of these compounds are stable in air, others absorb oxygen instantly; certain arseno compounds, indifferent toward oxygen, react instantly with the gas in the presence of traces of certain reagents. A number of aromatic arsenicals which contain an arsenic atom attached to arsenic or some other atom by a double bond are associated in the dissolved state.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MAGNETIC PIGMENT CO., TRENTON, N. J.]

SUBSTITUTION OF ONE ATOM OF NITROGEN FOR THREE ATOMS OF CHLORINE IN ORGANIC COMPOUNDS. I. ACTION OF AMMONIUM CHLORIDE ON BENZO-TRICHLORIDE

BY PETER FIREMAN

RECEIVED MARCH 19, 1930 PUBLISHED JULY 3, 1930

The present paper describes some work in continuation of an investigation begun more than a quarter of a century ago and of which the first contribution was published[1] in **1904.** The investigation was interrupted and has only lately been resumed.

While the first paper reported the results obtained from the study of the action of ammonium chloride on metallic chlorides, the present communication is concerned with the action of sal ammoniac on benzo-trichloride, is concerned with the beginning of a study of the substitution of one atom of nitrogen for three atoms of chlorine in organic compounds.

I. It was expected that benzo-trichloride and ammonium chloride when heated in a closed tube would react as follows

$$C_6H_5CCl_3 + NH_3HCl = C_6H_5CN + 4HCl$$

In accordance with the above equation monomolecular quantities of benzo-trichloride and ammonium chloride are required. I soon learned, however, that only with an excess of at least 60% of benzo-trichloride a smooth reaction takes place whereby all the ammonium chloride is used up in the formation of benzonitrile. The experiments here described were all carried out using such an excess of benzo-trichloride.

In the end the following procedure was adopted. The glass tubes contained each **2.14** g. **(4** mols) of ammonium chloride and **12.52** g. (6.4 mols) of benzo-trichloride. The heating took place between **210** and 220". Heating periods of four to six hours are convenient. As with the quantities of the reacting bodies indicated, nearly 6 g. sf hydrogen chloride was set

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[1] **Fireman,** THIS JOURNAL, 26, **741 (1904).**

free, a number of consecutive heatings of the same tube were required. The heating was discontinued when no more gas escaped. The final product is a thick liquid which becomes semi-solid on standing.

The product from 11 tubes, 77 g. in all, was subjected to distillation. Four fractions were separated weighing together 50.32 g. The first and fourth amounted to but a few cc. each. The first fraction went over below 182°, to which the temperature rose rapidly. The second fraction distilled over between 183 and 189°, mostly near the latter temperature. The third passed over at 189 to 197'. The fourth was collected up to 215'. The boiling point of benzonitrile is 190.6' and that of benzo-trichloride 214'. The nitrogen contents of the four fractions were, respectively, 7.2, 10.7, 12.19 and 10.6%. Thus benzonitrile predominated, as it contains, calculated, 13.59% of nitrogen. It was recognizable by its odor resembling that of bitter almond oil.

The residue in the flask, from which the benzonitrile and the benzotrichloride were distilled off, was solid and brown-black in color. A wider bent tube was now inserted and the distillation continued. A readily solidifying liquid went over at a temperature between 235 and 260°. It solidified in the short side tube and in a small beaker which served as a receiver. About 4 g. was collected of a readily melting substance. It was for the most part easily soluble in alcohol, leaving a small residue which was very sparingly soluble in this medium. The bulk of this fraction, upon a few recrystallizations, showed a melting point of 121° and was recognized as benzoic acid. Its formation was obviously due to the presence of moisture, which acted on benzo-trichloride during the heating in the closed tubes. The sparingly soluble fraction showed a melting point of 242.5' and so proved to be kyaphenine $(C_6H_5CN)_3$ as corroborated by a nitrogen determination.

A further fraction was separated from the residue by distillation under diminished pressure. For that purpose an Auschiitz distilling flask with a fused-on receiving tube was used. The distillation was carried out at 15-mm. down to 7-mm. pressure at temperatures of 265 to 335'. About 6 g. of a white, slightly yellowish product was obtained. This distillate was separated into two substances by boiling with alcohol. Copious quantities of the latter dissolved out a white substance, leaving the other, much larger in amount, exceedingly little soluble in that menstruum.

After repeated treatments with boiling alcohol a white powder was obtained which melted at 233° and proved to be kyaphenine $(C_6H_5CN)_3$.

The less difficultly alcohol-soluble white substance, upon recrystallization, shows a melting point of 269–270°. A combustion gave: C, 91.96; H, 6.67—indicating a hydrocarbon. A search in the "International Critical Tables" suggested tetraphenylmethane, with a melting point of 285° (corr.), as most nearly corresponding to the results obtained: calcd.

for $(C_6H_5)_4C$: C, 93.75; H, 6.25. Gomberg,[2] who was the first to prepare tetraphenylmethane, gave at first 272° as its melting point, later 280° and last 281.5–282°, which corrected is 285°. He crystallized this hydrocarbon from benzene, which when hot dissolves it freely. My white substance upon crystallization from benzene presented a network with occasional separate slender long crystals or sheaf-like formations of fine needles and now melted at 271°. I take it to be tetraphenylmethane containing a small admixture of kyaphenine. Its formation may have taken place according to the reaction

$$3C_6H_5CN + C_6H_5CCl_3 = (C_6H_5)_4C + 3CNCl$$

This supposition I intend to submit to an experimental test.

As a last residue, after all distillations, there remained a black lustrous substance which had solidified from a molten state.

II. The Reaction Autocatalytic.—Early in this investigation it was observed that on successive heatings and openings of the same tube, increasing quantities of hydrogen chloride were set free in equal periods of time. The following experiments, a few of many, will show this strikingly.

Though the heating was carried out in an ordinary bomb furnace of the Lothar Meyer type (with flaps at the ends), great care was used to make the successive heatings in each set of experiments as nearly alike as possible. The fluctuations of the temperatures in the middle of the furnace during the four-hour heatings rarely exceeded ± 1°.

On opening the tubes only a portion of the hydrogen chloride formed

TABLE I

HYDROGEN CHLORIDE LIBERATED

	Expt. at 215°		Expt. at 220°		Expt. at 210°
Period	Tube 1, g.	Tube 2, g.	Tube 1, g.	Tube 2, g.	Tube 1, g.
I	0.328	0.330	0.441	0.385	0.266
II	.457	.457	.562	.603	.371
III	.758	.600	.827	.895	.440
			(.107)[a]	(.108)[a]	
			(.515)[b]	(.565)[b]	
IV	.905	.832	1.915	1.972	.590
V	1.490	1.085	1.553	1.343	.740
VI	1.605	1.825			1.353
VII	0.565	0.888			1.380
VIII					0.783
Total HCl, g.	6.108	6.017	5.890	5.871	5.923

Calcd., 5.840 g.

[a] One of the four tubes heated at the same time exploded before 220° was reached (at 217°) causing discontinuance of the heating. [b] In resuming the heating, another tube exploded seventy-one minutes after 220° was reached.

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[2] Gomberg, ***Ber.***, 30, 2045 (1897); THIS JOURNAL, 20, 776 (1898); Gomberg and Berger, **Ber., 36,** 1909 (1903); Gomberg and Cone, *ibid.*, **39,** 1463 (1906).

rushes out. A number of days must be allowed the escape of gas for its entire removal. During that time considerable moisture is liable to enter the tubes. A calcium chloride tube was slipped over the tip to prevent this. All tubes were heated during four-hour periods, opened after each period and resealed again.

The growing speed in successive periods at once becomes evident. Obviously the increasing velocity of the reaction corresponds to the increasing accumulation of benzonitrile.

I am inclined to believe that the cause of benzonitrile serving as a catalytic agent is the ability of this nitrile to absorb hydrogen chloride. Benzonitrile seems to form a feeble compound with the latter under pressure greater than the atmospheric. This compound gradually decomposes on opening the tubes.

Summary

1. When benzo-trichloride and ammonium chloride are heated in a closed tube at about 200" and above, substitution of one atom of nitrogen for three atoms of chlorine takes place, with the formation of benzonitrile and hydrogen chloride.
2. All the nitrogen of ammonium chloride can be utilized for such a substitution only in the presence of an excess of at least 60% of benzo-trichloride.
3. A small part of the benzonitrile polymerizes to tribenzonitrile, or kyaphenine.
4. A small amount of tetraphenylmethane is also found as a product of the reaction.
5. The reaction is autocatalytic.

It may be noted that the substitution of nitrogen for chlorine in benzotrichloride is by no means a unique case. Already Liebig[3] through the action of gaseous ammonia and ammonium chloride on phosphorus pentachloride obtained "chlorophosphuret of nitrogen" which, as Gladstone and Holmes[4] later showed, had the composition $(PNCl_2)_3$. Also long ago Heintz[6] was able, by heating a solution of ammonia in absolute alcohol with chloroform at a temperature of 180–190°, to obtain at times ammonium cyanide, at times paracyanogen (CN),. Shortly later Cloez[6] found the following reaction to take place

$$CHBr_3 + 5NH_3 = NH_3HCN + 3NH_3HBr$$

TRENTON, NEW JERSEY

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[3] Liebig, *Ann.*, **11**, 146 (1834).

[4] Gladstone and Holmes, *J. Chem. Soc.*, [2] **2**, 225 (1864).

[5] Heintz, *Ann.*, **100**, 369 (1856).

[6] Cloëz, *Compt. rend.*, **46**, 348 (1858).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

THE IDENTIFICATION OF CARBONYL COMPOUNDS BY USE OF 2,4-DINITROPHENYLHYDRAZINE

BY CHARLES F. H. ALLEN

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In connection with another investigation under way in this Laboratory, use of the common reagents for a carbonyl group failed to give a solid derivative. At about the same time it was noted that there was no reliable rapid reagent for preparing solid derivatives of most of the aliphatic aldehydes and ketones. As a rule the reagents that form crystalline products with aromatic carbonyl compounds give oils with most of the corresponding aliphatic substances; in spite of this, Laboratory manuals in illustrating the preparation of characteristic derivatives, usually select their examples from the aromatic series.[1] Consequently when a decomposition product obtained in a research is an aliphatic carbonyl compound, as is frequently the case, the average student is at a loss as to a reliable method of identification. As a remedy, the use of substituted phenylhydrazines is often recommended; they have the disadvantages of a high cost or difficulty of preparation. After trying out several, we finally selected 2,4-dinitrophenylhydrazine as the one best meeting the above objections.

It can be prepared easily in the laboratory from inexpensive reagents by persons with slight experience. It gives good crystalline derivatives with most of the common aliphatic carbonyl compounds; if necessary, these solids are readily purified by recrystallization from alcohol. It can be used in the presence of water (*i. e.*, dilute solutions) in many instances.[2]

It seems strange that such a useful reagent is not more widely known. Probably this is because it was applied by its discoverers almost entirely to aromatic compounds,[3,4] which form crystalline products with phenylhydrazine itself, hence offered no particular advantage. Brady and Elsmire[5] call attention to its use with a few aliphatic aldehydes and one ketone, but their paper does not seem to have received the attention it deserves.

We have attempted to determine roughly the limits of its usefulness by applying it to all available carbonyl compounds. The results are shown

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[1] Adams and Johnson, "Elementary Laboratory Experiments in Organic Chemistry," The Macmillan Co., New York, 1928. Norris, "Experimental Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1924, 2d ed., p. 163; Cohen, "Practical Organic Chemistry," Macmillan and Co., Ltd., London, 1928; Noyes, "Organic Chemistry," Chemical Publishing Co., Easton, Pa., 4th ed., revised, 1920; Thorpe and Whiteley, "Student's Manual of Organic Chemical Analysis," Longmans, Greene and Co., Ltd., London, 1926.

[2] Kahlenberg, *Science*, 61, 344 (1925).

[3] Purgotti, *Gazz. chim. ital.*, 24, *I*, 555 (1894).

[4] Curtius and Dedichen, J. *prakt. Chem.*, [2] 50, 266 (1894).

[5] Brady and Elsmire, *Analyst*, 51, 77 (1926).

in the experimental part. The melting points of some derivatives are not far enough apart to be characteristic but this is of minor importance, since it is now customary to prepare a known sample for comparison and make a determination of a mixed melting point. A few substances did not give solid products—these are listed in the experimental part.

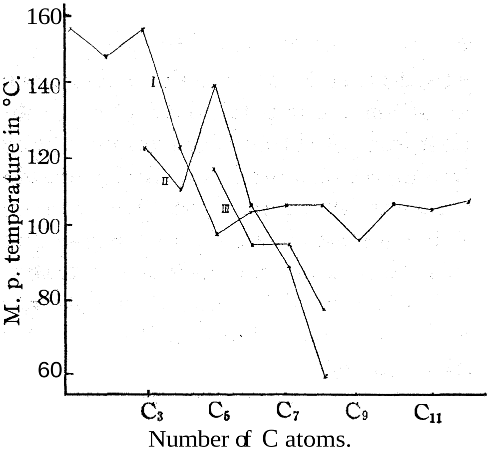

Fig. 1.

In the accompanying figure are shown the melting points of three series of dinitrophenylhydrazones plotted against the number of carbon atoms in the aliphatic part of the molecule. Curve I represents the straight-chain aldehydes, II the methyl ketones with a straight chain, and III the methyl ketones with a branched chain of the *iso* type (branching on the carbon atom farthest from the carbonyl group). The well-known alternating effect is noticeable, even though the series is short.[6]

Experimental

Preparation of **2,4-Dinitrophenylhydrazine.**—Fourteen g. of hydrazine sulfate is suspended in 50 cc. of hot water in a 125-cc. beaker, stirred well, and 35 g. of potassium acetate added to precipitate the sulfate as potassium sulfate. After boiling for five minutes, it is cooled somewhat and 30 cc. of alcohol added. When cold, the solid is filtered by suction and the cake washed while on the funnel with 25 cc. of hot alcohol. In a flask fitted with a reflux condenser and stirrer is dissolved 20.2 g. of technical 2,4-dinitrochlorobenzene in 100 cc. of alcohol, the hydrazine solution as prepared above is added and the whole refluxed with stirring for an hour. Most of the product crystallizes out after ten minutes. It is filtered, after cooling, and washed once with 25 cc. of warm alcohol to remove any unchanged dinitrochlorobenzene, and then with a small amount of warm water to remove soluble salts. By evaporating the filtrate to half its volume, a further 5 g. may be obtained, making the total yield 17 g. or 85%. The first crystals, m. p. 192°, are sufficiently pure for use as a reagent, but the last should be recrystallized from ethyl acetate.

Substitution of sodium hydroxide for potassium acetate slows up the reaction and gives an inferior product. This method avoids the preparation of concentrated solutions of hydrazine hydrate, though the latter gives a slightly better yield. The same yields can be secured with two and a half times the above amounts, if well stirred during the refluxing.

Of the several methods that can be devised for preparing 2.4-dinitrophenylhydrazones, we used the following.

A.—For qualitative identification of small amounts: A saturated solution of dinitrophenylhydrazine is prepared by refluxing 1 g. of the solid with 100 cc. of alcohol;

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[6] For example, cf. Malone and Reid, This Journal, 51, 3424 (1929).

it may partially crystallize on cooling. To **5** cc. of this solution (any suspended solid does no harm) in a test-tube is added **5** cc. of alcohol and a few drops of the carbonyl compound, and the whole carefully heated to boiling. After removing from the flame, **1–2** drops of concd. hydrochloric acid are slowly added; the color usually changes immediately to yellow or orange. The mixture is boiled for two minutes, and water added. drop by drop, to incipient cloudiness or crystallization. The dinitrophenylhydrazone is filtered after the solution is cold. If the aldehyde or ketone is fairly pure, recrystallization is unnecessary, but the products separating when commercial preparations are used are always impure. Alcohol is the best solvent for the low-melting derivatives, but the higher-melting less soluble compounds require the addition of ethyl acetate or chloroform. The dinitrophenylhydrazones of the simple ketones (except acetone and methyl ethyl ketone) separate slowly from alcohol, but usually form as oils on addition of water. If the solution is heated too long when acrolein is used, polymerization of some sort occurs and a viscous tar is precipitated.

B.—For preparing larger quantities, **2** g. of dinitrophenylhydrazine and a slight excess over the equivalent amount of carbonyl compound in **100** cc. of alcohol are heated to boiling, allowed to cool slightly and **2** cc. of concd. hydrochloricacid added. Usually the color changes at once, and any solid present dissolves. After boiling for two minutes, the solution is set aside until crystallization is complete, filtered by suction, washed with alcohol and recrystallized to constant melting point.

The reagent is not as useful when applied to α-hydroxy ketones of the acyloin and benzoin type; the formation of hydrazone is slow; unchanged material precipitates on addition of water. If the boiling is prolonged, oxidation takes place,[7] and the mixture of solid products formed is not easily separated by recrystallization. Since benzoin, benzil, and their homologs are solids this limitation is unimportant; however, not many crystalline derivatives of the liquid acyloins are known. After several recrystallizations a solid, m. p. 99°, was obtained from n-butyroin, but its structure is uncertain.[8]

It is essential that the carbonyl compounds be fairly pure; otherwise purification of the phenylhydrazones is difficult. For example, it was extremely difficult to purify the crystalline products formed from some samples of n-decylaldehydeand menthone.

The compounds used were either purchased from reliable sources or prepared by methods already in the literature.

TABLE I

RESULTS OF EXPERIMENTS

Ketones	M. p., °C.	Color	Aldehydes	M. p., °C.	Color
Acetone[4]	128	Y	Formaldehyde[3]	155	Y
Methyl ethyl[6]	115	Y	Acetaldehyde[3]	147	Y
Methyl n-propyl	141	YO	Propion-[5]	155	Y
Methyl n-butyl	106	RO	*n*-Butyr-[5]	122	Y
Methyl n-amyl	89	YO	Isobutyr-[5]	182	Y
Methyl *n*-hexyl	58	O	n-Valer-	98	Y
Methyl *n*-nonyl	63	OY	Isovaler-[5]	123	Y
Methyl n-undecyl	69	OY	Trimethylacet-[b]	210	Y
Methyl isopropyl	117	OY	*n*-Capro-[5]	104	Y
Methyl isobutyl	95	OR	*n*-Hept-[5]	106	Y
Methyl iso-amyl	95	O	n-Oct-	106	Y
Methyl isohexyl	77	OY	*n*-Nonyl-[5]	96	Y

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[7] Thus both piperoin and piperil give the same substance, m. p. **227".**

[8] Analysis for nitrogen gave **14.5** and **14.3,** whereas the calculated value for the monophenylhydrazone is 17.2%, and for the osazone 22.1%.

TABLE I (*Concluded*)

Ketones	M. p., °C.	Color	Aldehydes	M. p., °C.	Color
Pinacolone	125	OY	n-Decyl-	104	Y
Diethyl	156	WO	n-Undecyl-	104	Y
Di-n-propyl	75	YO	n-Duodecyl-	106	Y
Ethyl n-propyl	130	YO	Acrolein	165	RO
Ethyl isobutyl	75	YO	a-Methyl-0-ethyl acrolein	159	Carmine
Allylacetone	104	O	Citronellal	78	Y
Methylheptenone	81	RO	Citral I	108–110	RO
Pseudoionone	143	Deep red	Citral II	96	RO
Mesityl oxide	200	Carmine	a-n-Amylcinnamic aldehyde	164	Scarlet
Cyclopentanone	142	OY	**Acid derivatives**[c]		
Cyclohexanone[a]	160	OY	Pyruvic acid	213	Lemon
Methyl cyclohexyl	140	O	Levulinic acid	92	Y
Carvone	189	Carmine	Ethyl oxomalonate	128	Lemon
Menthone	145	O	Methyl benzoyl formate	171	OY
Benzalacetone	223	OR			
Benzalacetophenone	208	O			
Benzil[b]	185	OY			
Acetophenone	237	O			
α-Indanone	258	RO			
n-Butyroin	99	Y			
Benzoin	234	OY			

[a] This substance has previously been reported——ith m. p. 145°. [b] For this substance we are indebted to Mr. A. Paquet. [c] The reagent gives no precipitate with formic acid and the formates.

The results obtained with furoin, furil and benzfuroin were unsatisfactory. Furfural is reported to give a solid, m. p. 202°.[9] Anisoin, anisil, piperoin and piperil gave mixtures melting above 200°.

Representative samples were analyzed for nitrogen by the Kjeldahl method, on a semi-micro scale. A mixture made up of 0.030 g. of substance, 0.1 g. of copper sulfate, 2 g. of potassium sulfate, 2 g. of glucose and 15 cc. of concd. sulfuric acid was digested until colorless. After cooling, it was carefully diluted with 150 cc. of distilled water, a 24-g. stick of solid sodium hydroxide added, and the ammonia distilled in the usual manner. It was found most convenient to weigh the sample on a cigarette paper, and

TABLE II[a]

KJELDAHL ANALYSES

C=O compound	Nitrogen, % Calcd.	Found
n-Octaldehyde	18.1	18.3
Pinacolone	20.0	19.7
Methyl isohexyl ketone	18.1	18.1
Cyclohexanone	20.1	20.0
Citral II	16.5	16.5
Pseudoionone	15.1	14.9
α-*n*-Amylcinnamic aldehyde	14.9	15.1
Benzalacetone	14.5	14.7

[a] For these analyses we are indebted to Mr. D. D. McKay.

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[9] Ciusa, *Gazz. chim. ital.*, 41, 688 (1911); *Chem. Zentr.*, 82, 1644 (1911).

put the whole into the flask; of course, a paper was used in running a blank. Sodium hydroxide, **0.020** N and sulfuric acid, **0.040** *N* were of suitable strength. This method does not require as much skill as Pregl's micro method, nor as large a sample as the usual procedure. Senior students used it with good results.

2,4-Dinitrophenylhydrazine did not give solid derivatives with methyl n-heptyl, n-octyl, and n-decyl ketones, di-n-butyl ketone, commercial ionone, pure α-ionone, fenchone or pulegone.

Summary

1. An inexpensive method is given for the preparation of 2,4-dinitrophenylhydrazine.
2. This substance has been shown to be a suitable reagent to use in preparing crystalline derivatives of a large number of aliphatic compounds containing a carbonyl group. It may also be used with certain cyclic compounds, but the production of solid derivatives is not as general.
3. It is not as useful with a-hydroxyketones, owing to the difficulty in separating the mixtures formed.
4. A semi-micro method for determining nitrogen by the Kjeldahl method is outlined.

MONTREAL, CANADA

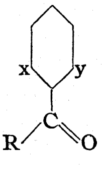
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STUDY OF THE POSSIBLE ISOMERISM OF CERTAIN ANALOGS OF RESOLVABLE DIPHENYL COMPOUNDS. VII[1]

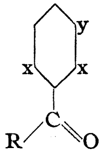
BY R. W. MAXWELL[2] AND ROGER ADAMS

RECEIVED MARCH 28, 1930 PUBLISHED JULY 3, 1930

It was pointed out in a previous paper[1a] that certain substances somewhat similar to diphenyl compounds might show the phenomenon of optical isomerism which exists in the ortho tri, and tetra-substituted members of the former class of compounds. These general types are given in formulas I to VI.



I



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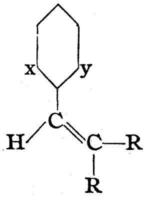

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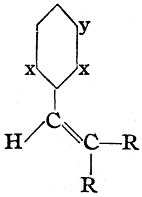

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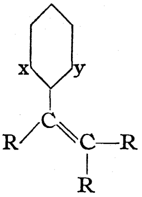

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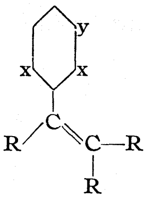

VI

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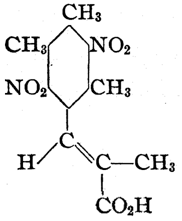
[1] For previous papers see (a) Hyde and Adams, THIS JOURNAL, 50, **2499** (1928); (b) Moyer and Adams, *ibid.*, 51, **630** (1929); (c) Stanley and Adams, *Rec. trav. chim.*, *48*, **1035** (1929); (d) Stanley and Adams, THIS JOURNAL, 52, **1200 (1930);** (e) Bock, Moyer and Adams, *ibid.*, 52, **2054 (1930);** (f) Stearns and Adams, *ibid.*, 52, **2070 (1930).**

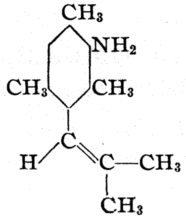
[2] This communication is a portion of an abstract of a thesis submitted by R. W. Maxwell in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

In the communication of Hyde and Adams,[1a] representatives of formulas I and II were prepared and shown not to be capable of resolution. In this paper compounds belonging to classes III and IV are described. Not one of them could be resolved. It is obvious then that there is in these compounds sufficient mobility of the groups around the carbon atom attached to the ring so that the ortho substituting groups have no blocking effect and free rotation between the ring and the carbon atom is not prevented.

The side chain must either be flexible or extend in such a direction that interference does not take place. Several attempts to prepare compounds of types V and VI have so far met with failure. In these latter compounds, analogy to trisubstituted diphenyl compounds is most complete and there is most likelihood that optical isomerism might be possible. The group replacing the side-chain hydrogen of III and IV corresponds to the unsubstituted ortho position which may play a part in preventing free rotation.

The particular compounds which were studied were α,3,4,6-tetramethyl-2,5-dinitrocinnamic acid (VII); amino-isobutenylmesitylene (VIII); and α-methyl-3-amino-2,4,6-tribromocinnamic acid (IX).


VII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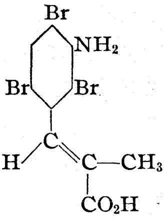
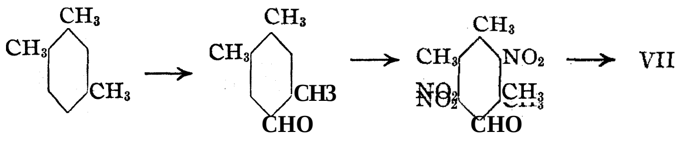
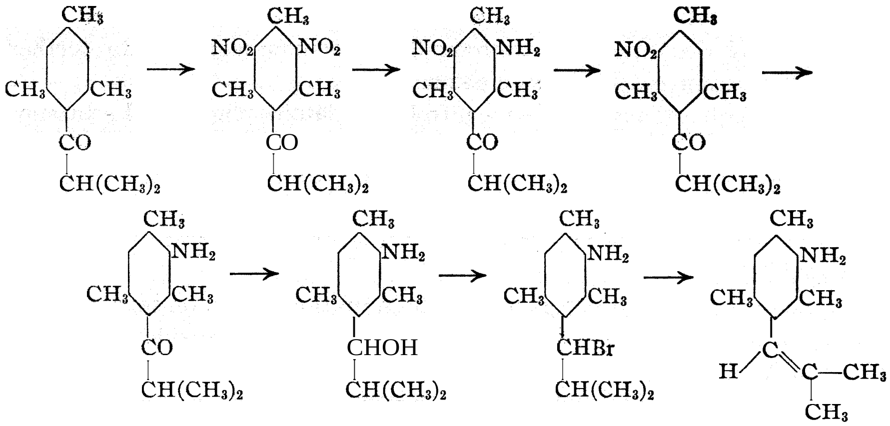

IX

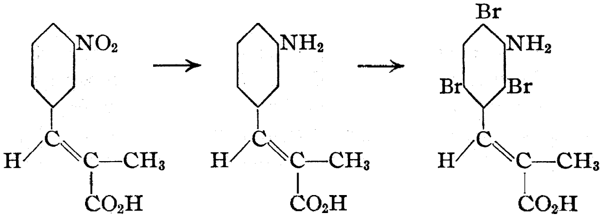
α,3,4,6-Tetramethyl-2,5-dinitrocinnamic acid was made by nitrating pseudocumenic aldehyde and then condensing with sodium propionate and propionic anhydride.



The amino-isobutenylmesitylene resulted from the following series of reactions: mesitylene, isobutyrylmesitylene, dinitro-isobutyrylmesitylene, nitro-amino-isobutyrylmesitylene, nitro-isobutyrylmesitylene, amino-isobutyrylmesitylene, isopropyl-(2,4,6-trimethyl-3-aminophenyl)-carbinol, isopropyl-(2,4,6-trimethyl-3-aminophenyl)-methyl bromide, amino-isobutenylmesitylene.



a-Methyl-3-amino-3,4,6-tribromocinnamic acid was obtained by condensation of *m*-nitrobenzaldehyde with propionic anhydride and sodium propionate, reduction of the nitro product to the corresponding amine and then bromination.



The unsuccessful attempts to prepare compounds of the types V and VI are described briefly below.

1. The condensation of 2,5-dinitro-3,4,6-trimethylacetophenone with malonic acid would not take place.

2. Ethyl α-phenyl-2,4,6-trimethylphenylacetate was readily prepared by esterification of the condensation product of a-bromophenylacetic acid with mesitylene. It was hoped to prepare a carbinol by means of excess. of Grignard reagent and then dehydrate to the desired product. The Grignard condensation, however, would not take place.

3. Desyl mesitylene, (w-phenyl-ω-(2,4,6-trimethylphenyl)-acetophenone) prepared by condensation of desyl chloride with mesitylene reacted with a large excess of phenylmagnesium bromide to give a small amount of tar but no carbinol.

4. Ethyl-a-methyl-3-nitrocinnamate readily formed a dibromide which by alcoholic potassium hydroxide gave α-methyl-β-bromo-3-nitrocinnamic acid. It was found that after reduction to the amino compound a product which was not very pure was obtained in which only two bromines entered the ring and probably only one in an ortho position.

5. Ethyl α-methyl-3-aminocinnamate was brominated in acetic acid to give ethyl α-methyl-2,4,6-tribromo-3-aminocinnamate but no further bromination occurred in the side chain.

6. 1 - (2,4,6 - trimethyl -3- *p* - nitrobenzoylaminophenyl) - 1 - bromo-2,2-dimethylethylene was produced from nitrobenzoylamino-isobutenylmesitylene by bromination and treatment of the product with pyridine. It was hoped that reduction of the nitro of the *p*-nitrobenzoyl residue might give a satisfactory resolving group but the salts formed were too readily hydrolyzed.

7. Isobutenylmesitylene gave upon bromination in carbon tetrachloride and subsequent treatment with alcoholic potassium hydroxide a dibromo compound with one bromine in the 3-position and the other in the beta position. It was found impossible, however, to introduce a salt-forming group.

8. Acetamino and carbo-ethoxyamino-isobutenylmesitylene could be converted to the β-bromo compound but it was found impossible to remove the acyl group without affecting the side chain.

Experimental

Bromo-m-xylene—A mixture of 106 g. of m-xylene, 100 g. of carbon tetrachloride and several iron nails was placed in a 500-cc. flask provided with a mercury-sealed stirrer, a dropping funnel and a condenser from which a tube led to the hood. The mixture was surrounded by an ice-bath, stirring commenced and 168 g. of bromine in 168 g. of carbon tetrachloride was added over a period of five hours. The flask was protected from the light by a towel. After standing for ten hours the red liquid was washed with water and 20% sodium hydroxide solution. The carbon tetrachloride was distilled off and the residue treated with 10 g. of sodium dissolved in 200 cc. of 95% ethyl alcohol to remove side-chain bromination products and hydrobromie acid. (The sodium ethylate was added cautiously to prevent a violent reaction.) This solution was heated to boiling for one hour and allowed to stand overnight. It was then diluted with much water and sufficient ether added to bring the oily layer to the top. The ethereal layer was washed thoroughly with water and dried with calcium chloride. The yield was 130 g. (70%) of material boiling at 200–205° (mostly 202–203°).

Pseudocumene.—This compound was prepared by a slight modification of the method of L. I. Smith[3] for the preparation of isodurene. A mixture of 20 g. of magnesium turnings, 37 g. of bromo-m-xylene, 1 g. of methyl iodide and 65 g. of dry ether was placed in a one-liter, three-necked flask provided with a mercury-sealed stirrer, dropping funnel and condenser. After the reaction had started 115 g. of bromo-m-xylene in 200 cc. of dry ether was run in at such a rate as to cause gentle refluxing. Stirring was continued for one hour after the magnesium had dissolved. Into the mixture was run 250 g. of freshly distilled dimethyl sulfate in 150 cc. of dry ether. Refluxing was continued with stirring for eight hours. The Grignard was then decomposed with dilute hydrochloric acid and water. The ether layer was washed three times with water to remove magnesium salts and then treated cautiously with sodium ethylate solution to remove any remaining dimethyl sulfate. When all danger of a vigorous reaction was over, the

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[3] L. I. Smith, "Organic Syntheses," 1931, John Wiley and Sons, Inc., New York, Vol. XI.

alkali and alcohol were washed out with water and the ether layer was dried over calcium chloride. The crude product was heated for three to four hours with 10 g. of sodium shavings to remove any remaining bromide, and then distilled with a free flame through a long column. The yield was 50-60 g. (50-60%), b. p. 165-170°.

2,5-Dinitro-3,4,6-trimethylcinnamic Acid.—A mixture of 4 g. of acetic anhydride, 1.2 g. of sodium acetate and 1.7 g. of 2,5-dinitro-3,4,6-trimethylbenzaldehyde (prepared from pseudocumene by the method of Gattermann[4]) was heated in a 50-cc. flask in an oil-bath at 140-150° for eight hours. The mixture was warmed with water and filtered. The residue was digested with 5% sodium carbonate solution and filtered. The two filtrates were poured into dilute hydrochloric acid solution. A slimy precipitate was formed which, after filtration and two crystallizations from dilute acetic acid, melted at 238-239° (corr.); yield, 1.2 g.

Anal. Calcd. for $C_{12}H_{12}N_2O_6$: C, 51.43; H, 4.29. Found: C, 51.10; H, 4.31.

α,3,4,6-Tetramethyl-2,5-dinitrocinnamic Acid.—A mixture of 12 g. of propionic anhydride, 3.5 g. of sodium propionate and 4.4 g. of 2,5-dinitro-3,4,6-trimethylbenzaldehyde was heated in an oil-bath at 160° for ten hours. The mixture was warmed with water until all propionic anhydride was destroyed and then made alkaline with 5% sodium carbonate. The solution was heated to boiling with decolorizing charcoal and filtered. On cooling, the sodium salt of the acid separated in golden plates. The suspension of the sodium salt was poured into dilute hydrochloric acid. A granular precipitate resulted which was crystallized first from 95% alcohol and then from glacial acetic acid. The product formed plates melting at 277-278° (corr.) and amounted to 2.75 g.

Anal. Calcd. for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.76. Found: C, 52.70; H, 4.71.

The acid does not add bromine on long standing in carbon tetrachloride solution in the dark.

Attempt to Resolve α,3,4,6-Tetramethyl-2,5-dinitrocinnamic Acid with Strychnine.—The salt was prepared by mixing an ethyl alcohol solution of 3.550 g. of strychnine with an ethyl alcohol solution of 3.128 g. of the acid. After standing for a short time no crystals appeared, so the solution was evaporated to a small volume. Vigorous agitation with a stirring rod caused crystals to form. The salt was redissolved in 200 cc. of hot ethyl alcohol, filtered and allowed to stand. Needle-shaped crystals soon appeared. These were filtered; weight, 1 g.

Rotation. 0.4070 g. made up to 20 cc. in chloroform gave $\alpha_D = -0.728°$; $l = 1$; $[\alpha]_D^{25}$ -17.9.

The filtrate was heated to dissolve a small amount of precipitated salt, filtered and allowed to stand until another crop of crystals separated; weight, 1.7 g., $[\alpha]_D^{25}$ -16.4. Successive crops of the salt from the filtrate gave the same rotation within experimental error. The amount of salt recovered was 97% of the theoretical. The first fraction melted at 145-149° (corr.).

Anal. Calcd. for $C_{34}H_{36}O_8N_4$: C, 65.0; H, 5.8. Found: C, 64.2; H, 6.1.

A chloroform solution of the salt was extracted with ammonium hydroxide. The ammonium salt solution so obtained was washed twice with chloroform and the rotation determined. The value obtained was zero.

Attempt to Resolve α,3,4,6-Tetramethyl-2,5-dinitrocinnamic Acid with Morphine.—The salt was prepared by mixing a methyl alcohol solution of 1.41 g. of morphine with a methyl alcohol solution of 1.37 g. of the acid. The solvent was evaporated from a steam-bath, the gummy residue dissolved in 35 cc. of a mixture of 70 parts of ethyl acetate and 30 parts of 95% ethyl alcohol and allowed to stand. The salt crystallized out in

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[4] Gattermann, Ann., 347, 375 (1906).

very stout needles. It was separated into fractions by filtering off and washing the crystals and allowing the filtrate and washings to stand until crystals formed again. The results of the fractionation are given below.

I. Weight 1.3 g., 0.097 g. made up to 20 cc. in 95% ethyl alcohol gave $\alpha_D = -0.590"$; $1 = 1$; $[\alpha]_D^{25}$ -60.8; M. p., 178–184° (corr.).

The successive fractions all gave the same rotation within experimental error. The first crystals obtained weighed 0.65 g. and gave $[\alpha]_D^{25}$ -61.8. The amount of salt recovered was 93.5% of the theoretical.

Anal. Calcd. for $C_{30}H_{33}O_9N_3$: C, 62.1; H, 5.70. Found: C, 61.6; H, 5.74.

Decomposition of the salt was effected by dissolving 0.3 g. in 10 cc. of hot 95% ethyl alcohol and pouring this solution into dilute hydrochloric acid. The acid separated as a fine powder. It was filtered by suction, washed with dilute hydrochloric acid and dissolved in 20 cc. of dilute ammonium hydroxide. The solution was optically inactive.

Attempt to Resolve α,3,4,6-Tetramethyl-2,5-dinitrocinnamic Acid with Brucine.—The salt was prepared by mixing an ethyl alcohol solution of 1.176 g. of the acid with an ethyl alcohol solution of 1.858 g. of crystallized brucine. The solution was evaporated to 100 cc. and allowed to stand. The salt crystallized as stout needles. These were filtered, washed with 95% ethyl alcohol and the filtrate allowed to stand until a new crop of crystals had formed. This was repeated until all of the compound had been deposited.

I. Weight, 1.8 g. This fraction was separated into an insoluble fraction, (a), weight, 0.75 g. 0.2215 g. made up to 15 cc. in ethyl acetate gave $\alpha_D = -0.347°$; $l = 1$; $[\alpha]_D^{25}$ -23.5, and a soluble fraction (b), $[\alpha]_D^{25}$ -18.4.

11. Weight, 0.5 g. $[\alpha]_D^{25}$ -22.7.

III. 0.5 g. (mother liquor), $[\alpha]_D^{25}$ -31.2.

The amount of recovered salt was 92.4% of the theoretical. Fraction (a) melted at 129–132" (corr.).

Anal. Calcd. for $C_{36}H_{40}O_{10}N_4 \cdot 2H_2O$: C, 59.64; H, 6.12. Found: C, 59.47; H, 6.07.

Anal. Subs., 0.6025: loss on heating at 110° for three hours, 0.0342. Calcd. for $C_{36}H_{40}O_{10}N_4 \cdot 2H_2O$: H_2O, 5.2. Pound: H_2O, 5.8.

The salt was decomposed by dissolving it in 10 cc. of warm ethyl alcohol and pouring this solution into dilute hydrochloric acid. The acid separated as a fine, white precipitate. It was washed with dilute hydrochloric acid, dissolved in dilute ammonium hydroxide and the rotation determined. The value obtained was zero.

Isobutyrylmesitylene.—Essentially the method of Klages[5] was used. A mixture of 107 g. of isobutyryl chloride, 120 g. of mesitylene and 500 cc. of dry carbon disulfide was placed in a one-liter, three-necked flask equipped with a mercury-sealed stirrer and a tube to carry off hydrogen chloride fumes. The flask was surrounded by an ice–salt mixture. To this was added 135 g. of anhydrous aluminum chloride in 10-g. portions over a period of one hour and fifteen minutes. After another hour and fifteen minutes the solvent was distilled off and the residue poured onto a mixture of ice and hydrochloric acid. The product was a brown oil. It was taken up in ether, washed with water and dilute sodium hydroxide, and dried with anhydrous magnesium sulfate. The product boiled at 122–126" at 7 mm. and amounted to 140 g. (75%).

Dinitro-isobutyrylmesitylene.—Twenty-eight grams of isobutyrylmesitylene was allowed to flow slowly into 200 g. of nitric acid (sp. gr. 1.52) cooled to −10". The time of addition was ten minutes and the acid temperature was not allowed to pass 15°.

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[5] Klages, *Ber.*, 37, 928 (1904).

Stirring was continued for five minutes more, after which the reaction mixture was poured into ice water. A longer time of contact with the acid was undesirable because of danger of side-chain nitration. The product precipitated as heavy crystals. It was filtered by suction, dried and recrystallized from 95% ethyl alcohol to a constant melting point 137.5–138.5°. The yield was 28 g.

Anal. Calcd. for $C_{13}H_{16}N_2O_5$: *C*, 55.7; H, 5.76. Found: C, 55.8; H, 5.86.

Nitro-amino-isobutyrylmesitylene.—To 250 g. of dinitro-isobutyrylmesitylene dissolved in 900 cc. of 95% ethyl alcohol was added a solution of 275 g. of crystallized sodium sulfide and 37 g. of sulfur in 750 cc. of water. The mixture was refluxed with stirring for six hours. It was then poured into four liters of water. The product separated as an oil which crystallized as the solution cooled. It was filtered and washed with water. The crude product was dissolved in hot 3 N hydrochloric acid and the solution filtered. On cooling, the hydrochloride separated as yellow plates. The free base was obtained by neutralization with ammonium hydroxide either from the solution of the hydrochloride or from the solid. It separated as an oil which soon crystallized in bright yellow needles. After purification from 95% ethyl alcohol it melted at 98–99° (corr.). The yield was 185 g.

Anal. Calcd. for $C_{13}H_{18}N_2O_3$: C, 62.4; H, 7.26. Found: C, 62.5; H, 7.26.

Nitro-isobutyrylmesitylene.—A solution was made of 100 g. of crude nitro-amino-isobutyrylmesitylene in a warm mixture of 90 cc. of concentrated sulfuric acid and 460 cc. of 95% ethyl alcohol. A 3-liter, three-necked flask equipped with a mercury-sealed stirrer, reflux condenser and dropping funnel was used. The solution was cooled to below 10° and 40 g. of sodium nitrite in 70 cc. of water allowed to run in slowly, care being taken that the temperature did not pass above 10°. Stirring was continued for twenty minutes after addition of the sodium nitrite in order to complete the diazotization. Ten grams of copper bronze freshly washed with ether was then stirred into the mixture. An evolution of gas commenced which proceeded for about thirty minutes. The flask was then placed upon a steam cone, warmed cautiously at first and then refluxed for half an hour. The boiling point was very low because of the acetaldehyde formed.

The contents of the flask were poured into two volumes of water, whereupon the product separated as a heavy brown oil. It was extracted with ether. The product boiled at 157–158° at 7 mm. and amounted to 31 g. A considerable quantity of tar always remained behind.

Anal. Calcd. for $C_{13}H_{17}NO_3$: C, 66.4; H, 7.28. Found: C, 65.9; H, 7.25.

Amino-isobutyrylmesitylene.—A mixture of 50 g. of mossy tin, 60 cc. of 95% ethyl alcohol and 32 g. of nitro-isobutyrylmesitylene was placed in a 500-cc. round-bottomed flask equipped with a reflux condenser. One hundred and twenty cc. of concentrated hydrochloric acid was added at such a rate that the temperature of the flask was kept just below the boiling point. After the reaction had apparently ceased, the contents of the flask were refluxed for fifteen minutes. There was no sign of hydrogen evolution during the reaction. The alcoholic solution was diluted with 300 cc. of water made alkaline with ammonia and filtered by suction. The filter cake of tin oxides was placed in a beaker, warmed with 250 cc. of 95% ethyl alcohol and filtered. This process was repeated and the filter cake washed thoroughly with warm alcohol. The alcoholic filtrate was added to one and one-half volumes of water and the precipitated oil separated from the water by extraction with ether. The product amounted to 24 g. and boiled at 167" at 7 mm.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.10; H, 9.27. Found: C, 75.69; H, 9.24.

Isopropyl **(2,4,6-Trimethyl-3-aminophenyl) Carbinol.**—To 41 g. of amino-isobutyrylmesitylene in 300 cc. of absolute ethyl alcohol in a 500-cc. round-bottomed flask equipped with a reflux condenser was added through the condenser 18.5 g. of sodium metal cut in small strips at such a rate that the alcohol refluxed gently. Toward the end of the reaction and for one hour after the last addition of the sodium the mixture was heated on a steam-bath. The solution was poured into two volumes of water. The product separated as a white, crystalline solid. It was extracted from the water with ether. The crystalline product was washed thoroughly with low-boiling petroleum ether. After recrystallizations from ligroin (b. p. 60–115°), the melting point was 118.5–119.5° (corr.). The yield was 22 g.

Anal. Calcd. for $C_{13}H_{21}NO$: C, 75.4; H, 10.2. Found: C, 75.1; H, 10.2.

Amino-isobutenylmesitylene.—A mixture of 48 g. of isopropyl-2,4,6-trimethyl-3-aminophenyl carbinol in 450 cc. of 40% hydrobromic acid was heated to boiling for several hours. The crystals which formed shortly after the reaction started melted, floated to the surface and resolidified in needles. Refluxing was continued for two hours, after which the contents of the flask were cooled and the product filtered. Without further purification the solid hydrobromide was mixed with a solution of 90 g. of potassium hydroxide in 500 cc. of 95% ethyl alcohol. An immediate precipitation of potassium bromide took place. The mixture was refluxed for half an hour and then poured into two volumes of water. A light oil separated. It was extracted from the water with ether. The product boiled at 127–128" at 6 mm. and amounted to 35 g.

Anal. Calcd. for $C_{13}H_{19}N$: C, 82.5; H, 10.1. Found: C, 82.2; H, 10.1.

Attempt to Resolve Amino-isobutenylmesitylene with d-Camphorsulfonic Acid.—The salt was formed by mixing 3.8 g. of the amine in 50 cc. of chloroform with 4.64 g. of d-camphorsulfonic acid. The acid dissolved slowly as the liquid was boiled. The solution was evaporated to about 10 cc. and 150 cc. of ligroin (b. p. 65–115°) added. This solution was allowed to stand where it could evaporate very slowly. After twenty-four hours silky needles were deposited but the solution was becoming very dark. The crystals were filtered and washed with a solution of 10 cc. of chloroform in 90 cc. of ligroin.

I. Weight, 1.0 g. 0.0985 g. made up to 15 cc. in chloroform gave $\alpha_D = +0.208°$; $1 = 1$; $[\alpha]_D^{25} + 32.0$.

The filtrate was allowed to stand as before. The solution became even more tarry. A second crop of crystals soon deposited.

11. Weight, 1.2 g. $[\alpha]_D^{25}$ +32.3.

The same procedure was carried out as before.

III. Weight, 1.3 g. $[\alpha]_D^{25}$ +27.3. The filtrate was now so dark and tar-like that no more crystals could be obtained. A portion of salt which had not been subjected to fractionation, however, gave $[\alpha]_D^{25}$ +34.2. The melting point of fraction I was 93–102° (corr.).

Anal. (Parr Bomb). Calcd. for $C_{23}H_{35}O_4SN$: S, 7.6. Found: S, 7.3.

The salt was decomposed by dissolving 0.25 g. in chloroform and extracting the solution with dilute ammonia. The resulting chloroform solution was optically inactive.

Attempt to Resolve **Amino-isobutenylmesitylene** with ***d*-Oxymethylenecamphor.**—A mixture of 1.36 g. of amino-isobutenylmesitylene and 1.5 g. of d-oxymethylenecamphor in 10 cc. of 95% ethyl alcohol was heated on a steam-bath for half an hour. To this was added 50 cc. of water containing 10 cc. of dilute sodium hydroxide to precipitate the condensation product and to dissolve excess d-oxymethylenecamphor. The product separated as a gum. On warming the alkaline mixture on a steam cone, the gum floated to the surface of the liquid and crystallized. The crystals were filtered off, washed and recrystallized from methyl alcohol. The following fractions were obtained.

I. Weight, 1.12 g., m. p. 176–180°. 0.1284 g. made up to 15 cc. in chloroform gave $\alpha_D = +4.7°$; $l = 1$; $[\alpha]^{25}_D$ +190.4.

11. Weight, 0.92 g. $[\alpha]^{25}_D$ +184.1.

III. Weight, 0.25 g. $[\alpha]^{25}_D$ +200.0.

Anal. Calcd. for $C_{24}H_{33}ON$: C, 82.0; H, 9.47. Found: C, 82.3; H, 9.46.

As the compound changed in rotation on standing, all readings were taken as nearly as possible at exactly ten minutes after the solution was made. The high rotation of fraction III is probably due to this. The amount of product recovered was 90.6% of the theoretical.

Attempts to decompose the condensation product with bromine in carbon tetrachloride followed by hydrolysis gave tarry products.

Acetamino-isobutyrylmesitylene.—A mixture of 8 g. of amino-isobutenylmesitylene and 30 cc. of acetic anhydride was allowed to stand for half an hour, after which the acetic anhydride was decomposed with cold water. After recrystallization from dilute alcohol the compound melts at 114–115°, resolidifies and remelts at 129–30° (corr.).

Anal. Calcd. for $C_{15}H_{21}NO$: C, 77.5; H, 9.16. Found: C, 77.3; H, 9.04.

a-Methyl-3-nitrocinnamic Acid.—The acid was prepared by a modification of the method of v. Miller and Rohde.[6] A mixture of 75 g. of m-nitrobenzaldehyde, 98 g. of propionic anhydride and 48 g. of sodium propionate was heated at 170° in an oil-bath for five hours. The reaction mixture was poured into water and saturated sodium carbonate solution added to strong alkalinity. The tarry liquid was boiled with decolorizing charcoal for ten minutes and then filtered. The alkaline liquid was poured into dilute hydrochloric acid. A white, curdy precipitate resulted. This was filtered by suction and allowed to dry overnight. The crude acid was crystallized once from 85% ethyl alcohol. The product consisted of white needles melting at 199.5–200.5° (corr.) and was used without further purification; yield, 70 g.

Ethyl a-Methyl-3-nitrocinnamate.—A mixture of 20 g. of a methyl-3-nitrocinnamic acid, 200 cc. of absolute alcohol and 6 g. of concentrated sulfuric acid was refluxed overnight. The solution was poured into two volumes of water. A heavy oil separated which did not crystallize on standing. It was extracted with ether. The product boiled at 197° at 11 mm. and amounted to 18 g.

Anal. Calcd. for $C_{12}H_{13}NO_4$: C, 61.3; H, 5.58. Found: C, 61.4; H, 5.59.

α-Methyl-3-amino-2,4,6-tribromocinnamic Acid.—A mixture of 20 g. of a-methyl-3-nitrocinnamic acid, 25 cc. of water, 100 g. of iron powder and 1 cc. of concentrated hydrochloric acid was placed in a 500-cc. flask and warmed upon a steam-bath for four hours. The contents of the flask were then made alkaline with ammonia, water was added and the mixture filtered. The residue on the filter was very thoroughly washed with water. The clear filtrates were poured into dilute hydrochloric acid, whereupon a slight precipitate separated. This was removed by filtration. To the acid solution was added 10% bromine in concentrated hydrochloric acid until a yellow color persisted. A curdy, white precipitate settled out. The precipitate of bromo acid was filtered by suction, dried in the air and recrystallized three times from 90% ethyl alcohol. Twenty grams of product melting at 208–209° (corr.) was obtained.

Anal. Calcd. for $C_{13}H_8NO_2Br_3$: Br, 58.0. Found: Br, 57.7.

Attempt to Resolve **a-Methyl-3-amino-2,4,6-tribromocinnamic** Acid **with** Strychnine.—To a solution of 4.14 g. of the acid in 25 cc. of warm methyl alcohol was added a solution of 1.67 g. of strychnine dissolved in 250 cc. of hot methyl alcohol. The solution was evaporated to 125 cc., filtered and allowed to stand until crystals were deposited. These were filtered by suction and washed well with methyl alcohol.

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[6] Miller and Rohde, *Ber.*, 23, 1900 (1890).

I. weight, 1.8 g. 0.2817 g. made up to 15 cc. in chloroform gave $\alpha_D = -0.451°$; $l = 1$; $[\alpha]^{25}_D$ −24.0.

To the filtrate was added 1.67 g. of strychnine dissolved in 250 cc. of methyl alcohol. The solution was again evaporated to 125 cc., filtered to remove a very fine precipitate which had formed and allowed to stand until another crop of crystals had appeared. The crystals were removed by filtration and the filtrate was allowed to stand until another crop was obtained.

II. Weight, 2.2 g. $[\alpha]^{25}_D$ −22.6.

III. Weight, 2.0 g. $[\alpha]^{25}_D$ −19.2.

IV. (Mother liquor), weight 1.3 g. $[\alpha]^{20}_D$ −20.6.

The amount of salt recovered was 98% of the theoretical. The melting point of fraction I was 123–127° (corr.).

Anal. Calcd. for $C_{31}H_{30}O_4N_3Br_3$: Br, 32.1. Found: Br, 31.7.

The salt was decomposed by dissolving a weighed portion in chloroform and extracting the chloroform with ammonium hydroxide. The solution of the ammonium salt was washed once with chloroform, and the rotation determined. The value obtained was zero.

Attempt to Resolve a-Methyl-3-amino-2,4,6-tribromocinnamic Acid with Brucine.—A mixture of 3.51 g. of crystallized brucine and 3.12 g. of a-methyl-3-amino-2,4,6-tribromocinnamic acid in 50 cc. of hot ethyl alcohol was evaporated to dryness on a steam cone, 300 cc. of water added and the mixture heated to boiling. The salt became crystalline under this treatment. The hot solution was filtered. Upon cooling 0.6 g. of white plates was deposited.

0.2953 g. made up to 15 cc. in ethyl acetate gave $\alpha_D = -0.55$; $l = 1$; $[\alpha]^{25}_D$ −28.2.

The residue from the water extraction was dissolved in 50 cc. of hot 95% ethyl alcohol and allowed to stand until crystals had appeared.

II. Weight, 4.0 g. $[\alpha]^{25}_D$ −30.4. This fraction was separated into three smaller fractions having specific rotations of −27.7, −31.2 and −31.2. A second crop of crystals was obtained from the filtrate from II.

III. Weight, 0.5 g. $[\alpha]^{25}_D$ −27.8. The mother liquor was evaporated to dryness.

IV. Weight, 1.5 g. $[\alpha]^{25}_D$ −39.4. The amount of salt recovered was 99.5% of the theoretical. The melting point of fraction I was 143–148° (corr.).

Anal. Calcd. for $C_{33}H_{34}O_6N_3Br_3$: Br, 29.7. Found: Br, 29.7.

The salt was decomposed by dissolving 0.25 g. in 10 cc. of 95% ethyl alcohol and pouring the solution into dilute hydrochloric acid. The precipitated acid was filtered washed with dilute hydrochloric acid, redissolved in dilute ammonium hydroxide, made up to 20 cc. and the rotation determined. The value found was zero.

Attempt to Resolve a-Methyl-3-amino-2,4,6-tribromocinnamic Acid with Quinine.—The quinine salt was prepared by dissolving 4.14 g. of the acid and 3.24 g. of quinine in 50 cc. of hot ethyl acetate and filtering. The filtrate was evaporated to 25 cc. and allowed to stand. Fine needles separated.

I. Weight, 0.7 g. 0.1750 g. made up to 15 cc. in ethyl acetate gave $\alpha_D = -0.69°$; $l = 1$; $[\alpha]^{25}_D$ −59.4.

The filtrate was set aside to crystallize again. This procedure was repeated until the salt had all separated. The six successive fractions obtained all gave rotations within experimental error of the first fraction. The amount of recovered salt was 93% of the theoretical. Fraction I melted at 208–209° (corr.).

Anal. Calcd. for $C_{30}H_{32}O_4N_3Br_3$: Br, 32.5. Found: Br, 32.0.

Decomposition of the salt was effected by shaking 0.25 g. of it in chloroform solution with dilute ammonium hydroxide and washing the ammoniacal solution twice with chloroform. The rotation of the salt so obtained was zero.

2,4,5-Trimethylacetophenone.—A mixture of 36 g. of pseudo-cumene, 90 g. of anhydrous aluminum chloride and 120 cc. of dry carbon disulfide was placed in a 1-liter, three-necked flask equipped with a reflux condenser, dropping funnel and mercury-sealed stirrer, The mixture was heated on a steam cone until gentle refluxing began and then 25 g. of acetic anhydride was allowed to flow in slowly from the dropping funnel. The time of addition was one hour. Refluxing was continued for another hour, after which the solvent was distilled from a steam-bath. The residue was poured into a mixture of ice and hydrochloric acid and the product extracted with ether. The product boiled at 121–124° at 5 mm.; yield, 36 g. (75%).

2,5-Dinitro-3,4,6-trimethylacetophenone.—Fifty grams of fuming nitric acid (sp. gr. 1.51) was cooled to –15° and 5 g. of 3,4,6-trimethylacetophenone added slowly with rapid stirring. Stirring was continued for ten minutes and then the mixture was poured into ice water. The product separated as a heavy oil. The oil was separated from the water by decantation and crystallized on standing. After several recrystallizations from 95% ethyl alcohol, it melted at 120–21° (corr.); yield. 1.4 g.

Anal. Calcd. for $C_{11}H_{12}O_5N_2$: C, 52.38; H, 4.77. Found: C, 52.25, 52.19; H, 4.40, 4.94.

Attempts to condense 2,5-dinitro-3,4,6-trimethylacetophenone with malonic acid by Knoevenagel's[7] method for acetophenone were unsuccessful.

α-Bromophenylacetic acid.—A mixture of 152 g. of mandelic acid. 60 g. of concentrated sulfuric acid and 350 g. of 48% hydrobromic acid was refluxed for four hours. The mixture first formed a liquid which floated on the surface of the acid but which soon became heavier and sank to the bottom. The product was extracted from the reaction mixture with 400 cc. of dry ether. The crude product after removal of solvent was a viscous, dark, clear oil. It was used directly for the next reaction.

α-(2,4,6-Trimethyl)-phenylacetic Acid.—The α bromophenylacetic acid from 1 mole of mandelic acid was placed in a 1-liter, three-necked flask equipped with a dropping funnel, mercury-sealed stirrer and reflux condenser. With it was mixed 400 cc. of dry carbon disulfide and 120 g. of mesitylene. Stirring was commenced and 135 g. of anhydrous aluminum chloride added in 10-g. portions in one hour. During this part of the reaction the flask was cooled by an ice-bath. Stirring was continued for another hour. The solvent was distilled from a steam-bath and the residue poured into a mixture of crushed ice and hydrochloric acid. The product separated as a viscous red-brown oil which soon crystallized. The crystals were filtered off, dissolved in benzene and the benzene extracted with dilute sodium hydroxide. The alkaline extract was allowed to run into dilute hydrochloric acid. The acid separated as a crystalline mass. It was filtered off, dissolved in hot 60% ethyl alcohol, decolorized with norite and set aside to crystallize. After several recrystallizations from 60% ethyl alcohol the melting point was 172–172.5° (corr.). The yield was 68 g. (27%) of white needles.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.31; H, 7.14. Found: C, 80.51; H, 7.12.

Ethyl **α-(2,4,6-Trimethylphenyl)-phenylacetate.**—Forty-three grams of α-(2,4,6-trimethylphenyl)-phenylacetic acid was dissolved in 250 cc. of absolute ethyl alcohol to which 2 cc. of concentrated sulfuric acid had been added. The mixture was refluxed for ten hours. The alcohol was then distilled off, the residue dissolved in low-boiling petroleum ether and the solution washed twice with water to remove sulfuric acid. After drying with anhydrous magnesium sulfate, the solvent was distilled from a steam-bath and the residue vacuum distilled. The ester boiled at 180–183° at 4 mm.; yield, 38 g. (81%).

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.85; H, 7.79. Found: C, 80.45; H, 7.69.

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[7] Knoevenagel, German Patent 162,281.

Ethyl α-(2,4,6-trimethylphenyl)-phenylacetate when treated with a large excess of phenylmagnesium bromide in the usual way gave a small quantity of an uncrystallizable tar but mostly unchanged material.

Desyl Chloride (Phenylbenzoylchloromethane.)—A mixture of 106 g. of benzoin and 72 g. of thionyl chloride was placed in a 500-cc. flask equipped with a reflux condenser. A reaction soon commenced. The mixture was allowed to stand without heating for two hours, at which time the reaction had almost stopped. The flask was then warmed on a steam cone for half an hour. The light brown liquid when cool was poured into water to decompose excess thionyl chloride. The product was extracted with ether. After washing and drying, the solvent was removed and the crude material used in the next reaction.

Desylmesitylene.—A mixture of 75 g. of mesitylene, 300 cc. of carbon disulfide and the crude desyl chloride from 0.5 mole of benzoin was placed in a 1-liter, three-necked flask equipped with a reflux condenser and mercury-sealed stirrer. The mixture was cooled by an ice-bath. Seventy-five grams of anhydrous aluminum chloride was added in 10-g. portions over a period of one hour. The solvent was distilled from a steam-bath and after cooling the residue was poured into a mixture of ice and hydrochloric acid. After standing for twelve to fifteen hours, the oily upper layer solidified. It was filtered off, dissolved in glacial acetic acid, boiled for fifteen minutes with norite, filtered and set aside to crystallize. After recrystallization to constant melting point from glacial acetic acid, the product melted at 111–112° (yield 63 g.).

Anal. Calcd. for $C_{23}H_{22}O$: C, 87.90; H, 7.01. Found: C, 87.53; H, 7.04.

Ethyl α-Methyl-3-nitrocinnamate Dibromide.—A mixture of 30 g. of ethyl α-methyl-3-nitrocinnamate and 125 cc. of glacial acetic acid was mixed with 125 cc. of glacial acetic acid containing 20 g. of bromine. After standing in the dark at room temperature for seventy-two hours, almost all of the bromine color had disappeared. The solution was poured into 1500 cc. of water and allowed to stand. Fine crystals separated slowly. After thirty-six hours these were filtered by suction. The product melted at 68–69° (corr.) after several recrystallizations from ligroin.

Anal. (Parr Bomb). Calcd. for $C_{12}H_{13}NO_4Br_2$: Br, 43.6. Found: Br, 43.4.

α-Methyl-β-bromo-3-nitrocinnamic Acid.—Sixteen grams of ethyl a methyl-3-nitrocinnamate dibromide was dissolved is 100 cc. of 95% ethyl alcohol and added to a solution of 8 g. of potassium hydroxide in 60 cc. of 95% ethyl alcohol. A precipitation of potassium bromide took place at once. The mixture was refluxed until completely water soluble (two to five minutes). The solution was poured into dilute hydrochloric acid. The acid separated in long silky needles, which after crystallization from benzene melted at 131.5–132.5° (yield, 10 g.).

Anal. (Parr Bomb). Calcd. for $C_{10}H_8O_4NBr$: Br, 28.0. Found: Br, 28.2.

Reduction with iron and water and bromination of the product gave an impure mixture.

Ethyl α-Methyl-2,4,6-tribromo-3-aminocinnamate.—A mixture of 12 g. of ethyl a-methyl-3-nitrocinnamate and 75 g. of iron powder was treated with sufficient water to form a thin paste. To this was added 0.5 cc. of concentrated hydrochloric acid and the mixture warmed on a steam cone under a reflux condenser for three hours. The reduction proceeded very rapidly at first, enough heat being generated to cause refluxing. The iron suspension was made faintly alkaline with ammonia, extracted thoroughly with warm alcohol and the extract filtered. The filtrate was poured into cold water. A heavy oil separated. It was removed from the water by ether extraction. The ether was washed, dried and distilled from a steam-bath and the residue used in the next reaction without further purification; yield, 10 g.

The crude ester was dissolved in 75 g. of glacial acetic acid and mixed with 32 g. of bromine in 75 g. of glacial acetic acid. It was necessary to cool the solution as the bromine was added. The mixture was allowed to stand in the dark for three days. A mass of white crystals separated in the meantime. These were filtered and the filtrate poured into cold water. A gum separated which crystallized slowly. The white residue on the filter was recrystallized several times from 95% ethyl alcohol. The same product was obtained upon crystallizing the gummy precipitate. The compound, when pure, melted at 107.5–108° (corr.).

Anal. (Parr Bomb). Calcd. for $C_{10}H_8O_2NBr_3$: Br, 54.3. Found: Br, 54.7.

1-(2,4,6-Trimethyl-3-*p*-nitrobenzoylaminophenyl)-1-bromo-2,2-dimethylethylene.—A mixture of 3.5 g. of amino-isobutenylmesitylene and a solution of 5 g. of *p*-nitrobenzoyl chloride in 25 cc. of benzene was allowed to stand for two hours. Dilute sodium hydroxide was then added and the benzene boiled off from a hot-plate. The product was left as a gum which soon crystallized. After one crystallization from alcohol it melted at 164-155° (uncorr.).

The product from the above reaction was dissolved in 100 cc. of glacial acetic acid and 32 g. of a 10% solution of bromine in glacial acetic acid allowed to flow in over a period of fifteen minutes with rapid stirring. A faint trace of hydrogen bromide was evolved. The solution was allowed to stand for ten minutes and was then poured into two volumes of water and allowed to stand overnight. The precipitate coagulated completely by that time. The product was filtered by suction, dried in the air, dissolved in 75 cc. of pyridine and refluxed for three hours. (The pyridine might be replaced by alcoholic alkali if the theoretical quantity were used. In one experiment an excess of alcoholic alkali caused tar formation.) The solution was poured into 500 cc. of water. A white cloudiness appeared and the solution began to deposit droplets which crystallized slowly. The mixture was stirred for four hours to aid crystallization and then the crystals were filtered by suction, washed well with water and dried. The crude product weighed 4 g. It was recrystallized from 95% ethyl alcohol and gave needles melting at 203.5–204.5° (corr.).

Anal. (Parr Bomb). Calcd. for $C_{20}H_{21}N_2O_3Br$: Br, 19.2. Found: Br, 18.9.

2,4,6-Trimethylphenylisopropyl Carbinol.—This compound was prepared by the reduction of the ketone by means of sodium and absolute alcohol. It boiled at 126° at 5 mm. (yield, 53 g., from 70 g. of ketone).

Isobutenylmesitylene.—This compound has been prepared by Klages[5] by decomposing 2,4,6-trimethylphenylisopropylmethyl chloride with pyridine. A mixture of 94 g. of 2,4,6-trimethylphenylisopropyl carbinol and 20 cc. of toluene was placed in a 200-cc., round-bottomed flask equipped with a reflux condenser. The flask was placed in an ice-bath and 55 g. of phosphorus tribromide allowed to run in slowly. After standing for one hour with occasional shaking and then heating for one hour on the steam cone, it was cooled and poured into cold water to decompose any phosphorus tribromide. The product was extracted with ether. After removing the solvent, 80 g. of potassium hydroxide in 450 cc. of 95% ethyl alcohol was added and the mixture refluxed for one hour. The solution became red and much potassium bromide separated. The alcohol suspension was poured into water and the product extracted with ether. The solvent was distilled from a steam cone and the olefin vacuum distilled. It boiled at 103-106" at 5 mm. (yield, 75 g.).

1-(2,4,6-Trimethyl-3-bromophenyl)-1-bromo-2,2-dimethylethylene.—A solution of 45 g. of carbon tetrachloride was allowed to flow into 29 g. of isobutenylmesitylene (thirty minutes) dissolved in 29 g. of carbon tetrachloride and cooled by an ice-bath. The mixture was stirred vigorously. After two and one-half hours a small amount of bromine had not reacted. The liquid was washed with water, dilute sodium hydroxide and then twice more with water. The bulk of the solvent was distilled from a steam-bath and the last traces from an oil-bath. At about 160° bath temperature, hydrogen bromide fumes were evolved copiously. The residue in the flask was added to a solution of 30 g. of potassium hydroxide dissolved in 175 cc. of 95% ethyl alcohol and refluxed for one hour. The reaction mixture was poured into cold water and the product extracted with ether. After purification by distillation, **27** g. of bromo compound boiling at **140–145**° at **4** mm. was obtained.

Anal. (Parr Bomb). Calcd. for $C_{13}H_{16}Br_2$: Br, 48.2. Found: Br, **47.8.**

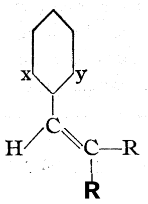
The mono Grignard reagent formed from the above compound, when treated with carbon dioxide, gave an acid which did not crystallize.

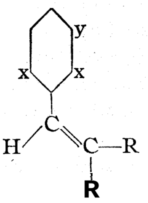
Amino-isobutenylmesitylene when brominated in either glacial acetic acid or carbon tetrachloride gave mostly tarry products. The acetylamino and carbo-ethoxyamino derivatives brominated in a satisfactory manner and gave a good-looking product upon removal of hydrogen bromide by alcoholic potassium hydroxide. It was found impossible, however, to remove the protecting group without affecting the unsaturated side chain.

Summary

1. α,3,4,6-Tetramethyl-2,5-dinitrocinnamic acid, amino-isobutenyl mesitylene and α-methyl-3-amino-2,4,6-tribromocinnamic acid have been prepared. They could not be resolved.

2. These substances are representative of the following two types:





It may be concluded that these compounds stereochemically do not resemble diphenyl compounds.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE REARRANGEMENT OF ACETYLCHLORO-AMINOBENZENE

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The properties of acetylchloro-aminobenzene have been under investigation, intermittently, for more than forty years[1] but the mechanism whereby it is converted into o- and *p*-chloro-acetanilide has not yet been definitely established. The plan outlined by Orton and his associates has been generally accepted but it fails to account for some of our observations. As envisaged by Orton and others, the first step in the process is a reversible reaction between acetylchloro-aminobenzene and hydrogen chloride which gives rise to acetanilide and chlorine. This is followed by an irreversible chlorination of acetanilide.

$$C_6H_5NAcCl + HCl \rightleftharpoons C_6H_5NAcH + Cl_2 \qquad (A)$$
$$C_6H_5NAcH + Cl_2 \longrightarrow ClC_6H_4NAcH + HCl \qquad (B)$$

When acetanilide is added to an acetic acid solution of acetylchloro-aminobenzene and hydrogen chloride, the rate of the reaction increases but reaches a maximum after a certain definite concentration of acetanilide has been added.[2] This is explained by Soper as being due to the fact that "in the mixture of chloro-amine and hydrochloric acid, the chlorine when formed undergoes two main and simultaneous reactions, (a) with the acetanilide forming o- and p-chloro-anilides and (b) with the chloro-anilides, which are present at a much higher concentration than acetanilide, forming chloro-amines. These chloro-amines of the chloro-anilides are formed progressively and since they contribute to the iodine titer, the observed rate of fall of iodine titer is less than that of the formation of chlorine in reaction A. When excess of some readily C-chlorinatable substance is present, competition for the chlorine reduces the N-chlorination of the chloro-anilides to a negligible amount and the rate of fall of titer increases to a constant value equal to that of the formation of chlorine."[3]

If this mechanism were correct the addition of chlorine should produce a change in the rate of disappearance of active'chlorine similar to that caused by the addition of acetanilide, for this would insure the removal of the acetanilide as fast as formed in Equation A. We found the effect of chlorine to be entirely different from that of acetanilide. Moreover, on

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[1] Bender, *Ber.*, **19**, 2272 (1886); Slosson, *ibid.*, 28, 3265 (1895); Chattaway and Orton, J. *Chem. Soc.*, 75, 1046 (1899); Armstrong, *ibid.*, **77**, 1047 (1900); Mathews and Williamson, THIS JOURNAL, 45,2574 (1923); Blanksma, *Rec. trav. chim.*, 21,290 (1902); Acree and Johnson, *Am. Chem.* J.,38, 258 (1907); Porter and Wilbur, THIS JOURNAL, 49, 2145 (1927); Orton, Soper and Williams, *J. Chem. Soc.*, 998 (1928); Richardson and Soper, *ibid.*, 1873 (1929); Williams, *ibid.*, 37 (1930); Belton, *ibid.*, 116 (1930).

[2] Orton and Jones, *British Assocn. Advancement Sci. Repts.*, 1910, p. 86.

[3] Soper, J. *Phys. Chem.*, 31, 1193 (1927).

the basis of the above explanation, the maximum rate obtainabie by adding acetanilide should not be exceeded by the substitution of any other amide. We have found that the use of β-acetnaphthalide causes the disappearance of the chloro-amine at a rate exceeding the maximum rate attainable with acetanilide.

The rearrangement of acetylchloro-aminobenzene is catalyzed by hydrogen chloride and since side reactions result in the accumulation of hydrogen chloride the reaction appears to be autocatalytic. In order to maintain constant hydrogen-ion and chloride-ion concentrations, sodium acetate and sodium chloride were used as buffers. The solubility of sodium chloride in a 0.05 M solution of sodium acetate in glacial acetic acid is 0.015 mole per liter at 40°. In 0.02 M sodium acetate solution the solubility of sodium chloride is 0.017 mole per liter at 40°. With solid sodium chloride present a constant concentration of chloride ion was maintained. With sodium acetate present the hydrogen-ion concentration was held at a constant value. The solvent used in every experiment was glacial acetic acid.

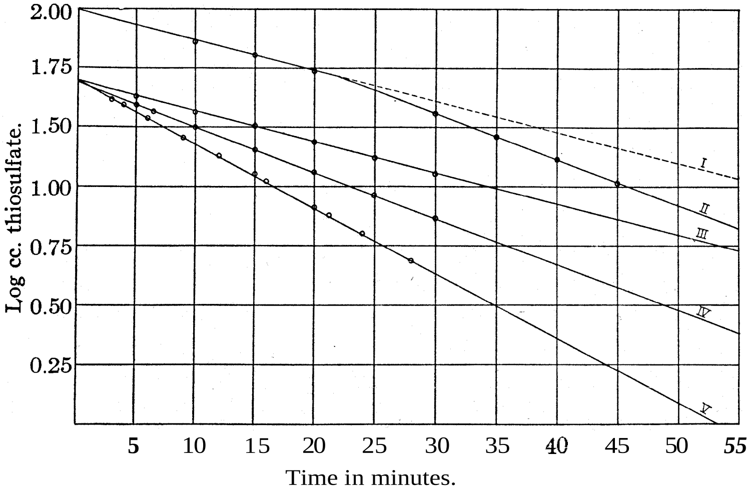

Fig. 1.—Each curve represents a rate of disappearance of active chlorine. In each case the acetylchloro-aminobenzene was dissolved in glacial acetic acid containing sodium acetate (0.05 M) and saturated with sodium chloride. The temperature was 40°. Curve I, 0.1 M acetylchloro-aminobenzene alone. Curve II, same as I at the beginning but twenty-five minutes later acetanilide was added in sufficient quantity to produce the maximum rate attainable with this reagent. Curve III, 0.05 M acetylchloro-aminobenzene (same as I but with one-half as much chloro-amine). Curve IV, 0.05 M acetylchloro-aminobenzene and 0.05 M acetanilide. Curve V, 0.05 M acetylchloro-aminobenzene and 0.05 M β-acetnaphthalide.

The rates of the reaction in the presence of varying quantities of acetanilide and of other amides are shown graphically in Fig. 1. The slope of Curve I represents the uncatalyzed rate. Curve III also represents this rate. Different concentrations of the chloro-amine were used in the two cases but it will be observed that the lines are parallel. Curve IV and the last half of Curve II show the maximum rate attainable with acetanilide added, and Curve V shows the maximum rate obtainable by adding β-acetnaphthalide. The slope of Curve V is steeper than that of IV. We believe that these anilides are chlorinated directly by acetylchloro-aminobenzene and that the formation of free chlorine is not a necessary antecedent. This, however, fails to explain the fact that maximum rates are reached with various chlorine acceptors.

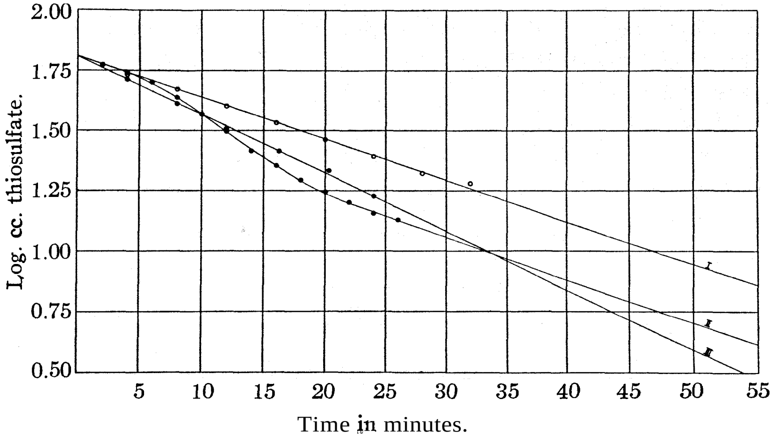

Fig. 2.—The solvent in each case was glacial acetic acid saturated with sodium chloride and 0.02 M with respect to sodium acetate. The temperature was 40°. Curve I, 0.06 M acetylchloro-aminobenzene alone. Curve II, 0.05 M acetylchloro-aminobenzene and enough chlorine added to make the initial titration approximately equal to that of a 0.06 M solution of the chloro-amine. Curve III, 0.06 acetylchloro-aminobenzene and an excess of acetanilide.

The addition of chlorine instead of acetanilide does not increase the rate of disappearance of chlorine at once. For a short time the normal products of the rearrangement are formed at the uncatalyzed rate. This is followed by a rapid reaction in which the chlorine is used and finally the rate falls to that of the original uncatalyzed reaction. The course of the reaction with chlorine added is shown by Curve II in Fig. 2. We assume that free chlorine acts rapidly upon acetanilide and upon o- and p-chloro-acetanilide but very slowly or not at all upon an N-chlorinated anilide. The added free chlorine, therefore, has no appreciable influence until acetanilide or a rearrangement product of acetylchloro-aminobenzene appears. It acts rapidly upon these compounds, substituting chlorine in the ring. When the added chlorine has been removed the rate returns to the uncatalyzed value. The slope of the curve during the period when the chlorine is being removed exceeds that of the maximum rate produced by the addition of acetanilide.

We are unable to harmonize the effects shown in Figs. 1 and 2 with the current theory of the rearrangement. On the other hand, we have no thoroughly satisfactory mechanism to offer as a substitute.

Summary

In glacial acetic acid containing sodium chloride and sodium acetate as buffers, the rearrangement of acetylchloro-aminobenzene is a first-order reaction. The rate of disappearance of the chloro-amine is accelerated by the addition of acetanilide or β-acetnaphthalide. In each case a maximum rate can be secured but the maximum rates produced by the two amides are not identical.

The addition of chlorine and of acetanilide have entirely different effects upon the rate of the reaction. These results are not in harmony with the view that the first step, and the slowest one, is the reversible production of chlorine and acetanilide from the chloro-amine and hydrochloric acid,

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

TETRACYCLOHEXYLDIPHENYLETHANE

BY S. S. ROSSANDER, L. H. BOCK AND C. S. MARVEL

RECEIVED APRIL 2, 1930 PUBLISHED JULY 3, 1930

In recent years it has been shown that the cyclohexyl group is effective in promoting the dissociation of hexa-substituted ethanes. Ziegler and Schnell[1] have prepared dicyclohexyltetraphenylethane and found that it forms a peroxide in the air. Conant and his students[2] have observed that dicyclohexyldixanthyl is dissociated into the free radical cyclohexylxanthyl to a considerable extent. These facts make it desirable to know the properties of ethanes which have more than two cyclohexyl groups in the molecule.

Some time ago Gray with Marvel[3] reported the preparation of a hydrocarbon, which they believed to be tetracyclohexyldiphenylethane, by the action of silver on a boiling toluene solution of dicyclohexylphenylchloromethane. Later Conant, Small and Sloan[2b] showed that this hydrocarbon was in reality phenylcyclohexylidinecyclohexylmethane. In view

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[1] Ziegler and Schnell, Ann., 437, 252 (1924).

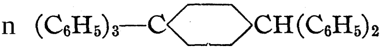
[2] (a) Conant and Small, THIS JOURNAL, 47, 3068 (1925); (b) Conant, Small and Sloan, *ibid.*, 48, 1743 (1926).

[3] Gray with Marvel, *ibid.*, 47, 2796 (1925).

of the great interest in the properties of a hexa-substituted ethane containing two cyclohexyl groups on each ethane carbon, this preparation has been undertaken again.

It was found in the present work that dicyclohexylphenylchloromethane would react with 40% sodium amalgam to give a red metallic alkyl along with a hydrocarbon which from its analysis proved to be an isomer of the desired tetracyclohexyldiphenylethane. When the pure sodium alkyl was treated with tetramethylethylene bromide in ether solution according to the procedure developed by Ziegler and Schnell,[4] the color disappeared. The colorless ether solution reacted with either 1 or 40% sodium amalgam to give again the original metallic alkyl. The ether solution absorbed oxygen with some rapidity. When air was rapidly bubbled through the ether solution, a white crystalline solid separated and this on analysis proved to be dicyclohexylphenylmethyl peroxide. These reactions all indicate that tetracyclohexyldiphenylethane was present in this ether solution and that it was to some extent dissociated into a free radical.

In order to be certain of the structure of the compounds which were obtained, the dicyclohexylphenylmethyl sodium prepared from the dicyclohexylphenylchloromethane was converted into dicyclohexylphenylacetic acid. The same acid was obtained by cleavage of the unstable hydrocarbon with sodium amalgam and treatment of the alkali metal alkyl thus obtained with carbon dioxide. This acid on oxidation yielded benzoic acid. Hence there had been no rearrangement of the metal into the benzene ring as sometimes occurs with benzyl halides in reactions of this type. With water the metallic alkyl gave dicylohexylphenylmethane.

No method has yet been devised for the isolation of the unstable hydrocarbon in a pure condition. It readily rearranged on heating or on standing when exposed to the light. This rearrangement with heat produced the isomeric hydrocarbon which was obtained by the action of sodium amalgam on dicyclohexylphenylchloromethane. The stable rearranged hydrocarbon probably has a structure analogous to that of the hydrocarbon  which is formed by the rearrangement of hexaphenylethane.[5]

The peroxide reacted with sulfuric acid to give dicylohexylphenylcarbinol. The carbinol was identified by converting it to dicyclohexylphenylchloromethane by treatment with acetyl chloride. This chloride had the proper melting point and showed no depression when a mixed melting point was taken with an authentic specimen of the chloride.

The reactions which have been carried out may be seen in the diagram.

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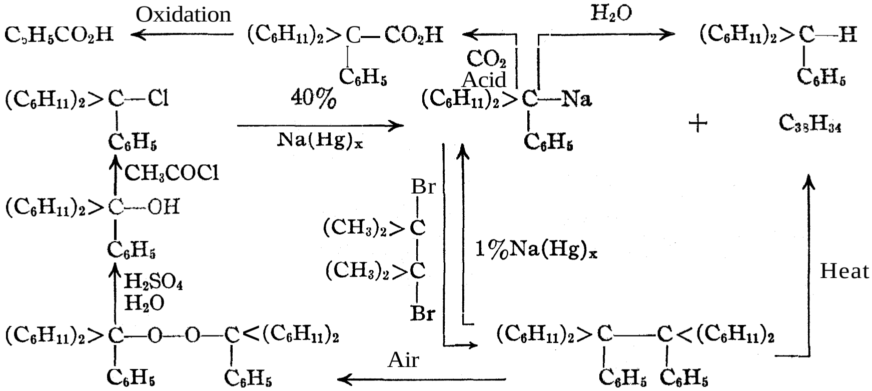
[4] Ziegler and Schnell, Ann., **437**, 244 (1924).

[5] Gomberg, Ber., 36, 379 (1903); Tschitschibabin, *ibid.*, **37**, 4709 (1904); **41**, 2421 (1908); Schlenk and Marcus, *ibid.*, **47**, 1665 (1914).



Experimental Part

Dicyclohexylphenylchloromethane was prepared as described by Gray with Marvel.[3]

Dicyclohexylphenylbromomethane.—To a solution of 14 g. of dicyclohexylphenylcarbinol in 40 cc. of dry benzene was added 10 cc. of acetyl bromide. The solution was allowed to stand overnight and the solvent was removed by evaporation under reduced pressure until crystals began to appear. At this point 100 cc. of 95% alcohol was added and the mixture was cooled overnight in an ice box. After three crystallizations from benzene and alcohol there was obtained 10–12 g. of a product which melted at 104–105°.

Anal. Subs., 0.3321: 13.2 cc. of 0.07504 N $AgNO_3$. Calcd. for $C_{19}H_{27}Br$: Br, 23.86. Found: Br, 23.91.

An attempt to prepare the Grignard reagent from the bromide was unsuccessful. Silver would not remove the bromine from the molecule in cold toluene solution. It was observed that heating either the chloro compound or the bromo compound in toluene solution gave phenylcyclohexylidinecyclohexylmethane and halogen acid.

Sodium Dicyclohexylphenylmethyl *and the Hydrocarbon* $C_{38}H_{54}$.—A solution of 5 g. of dicyclohexylphenylchloromethane in 100 cc. of anhydrous ether was placed in a 500-cc. round-bottomed flask and the air was swept out with nitrogen. To this solution was added 40 cc. of 40% sodium amalgam. The flask was tightly stoppered, placed on a shaking machine and agitated for about eight hours. A red color developed in about an hour. At the end of the shaking period the excess amalgam was frozen by cooling the mixture in an ice-bath and the solution of the metallic alkyl was transferred to a second flask. During this process and subsequent operations an atmosphere of dry nitrogen was maintained over the reaction mixture. To the suspension 100 cc. of dry, oxygen-free petroleum ether (b. p. 25–65°) was added in order to precipitate any of the metallic derivative from the ether. A cloth filter was fitted into the neck of the flask and the flask was inverted. The ether solution was then filtered. The red metallic alkyl remained on the filter.

The ether solution which was filtered from this reaction mixture was evaporated. The residue was recrystallized with some difficulty from benzene and alcohol. It melted at 209–211°.

Anal. Subs., 0.1310: CO_2, 0.4283; H_2O, 0.1254. Calcd. for $C_{38}H_{54}$: C, 89.33; H, 10.67. Found: C, 89.17; H, 10.70. Mol. wt. (in benzene) Subs., 0.3893: benzene, 21.975; At, 0.191°. Calcd. for $C_{38}H_{54}$; mol. wt., 510. Found: mol. wt., 475.

This hydrocarbon was very stable. It could be heated to 220° at 1 mm. without decomposition. When 1 g. of hydrocarbon was boiled with 100 cc. of aqueous potassium permanganate solution for twelve hours, over half of it was recovered unchanged. Oxidation with potassium dichromate and sulfuric acid destroyed the compound entirely. The hydrocarbon was unaffected by liquid sodium–potassium alloy.

Dicyclohexylphenylacetic Acid.—The sodium dicyclohexylphenylmethyl obtained from 6 g. of the chloride as described above was suspended in 50 cc. of ether (freshly dried with ethylmagnesium bromide) and dry carbon dioxide was passed into the suspension for about ten minutes. To the mixture was slowly added, first, about 15 cc. of water and then a solution of 5 g. of sodium hydroxide in 30 cc. of water. The mixture was warmed on the water-bath to remove the ether and 10 cc. of alcohol was added. This solution was cooled to about $-5°$ and acidified with dilute hydrochloric acid. The acid which separated was recrystallized twice from glacial acetic acid and then melted at 242–244°. The yield was 0.9–1.1 g.

Anal. Subs., 0.1270: CO_2, 0.3738; H_2O, 0.1070. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.40. Found: C, 80.20; H, 9.43. Subs., 0.092: 9.75 cc. of 0.0312 N NaOH. Calcd. for $C_{20}H_{28}O_2$: neutral equivalent, 300.2. Found: 302.

Three and one-quarter grams of the acid was boiled under a reflux condenser with an aqueous solution of 20 g. of potassium permanganate for four hours. An additional 27 g. of potassium permanganate was then added and the solution was again boiled under a reflux condenser for eight hours. The excess permanganate was destroyed by alcohol and the reaction mixture was worked up as usual. From the mixture was obtained about 0.25 g. of benzoic acid, m. p. 119–120°. A mixed melting point with an authentic specimen of benzoic acid showed no depression.

Dicyclohexylphenylmethane.—The pure sodium dicyclohexylphenylmethyl from 30 g. of dicyclohexylphenylchloromethane was suspended in ether and treated with water from which the dissolved oxygen had been removed. The ether was evaporated and the remaining oil was distilled under reduced pressure. The product boiled at 145–148° at 5 mm. The yield was 10 g., n_D^{20} 1.5390.

For comparison the same hydrocarbon was prepared by the reduction of phenylcyclohexylidenecyclohexylmethane. To a solution of 17 g. of phenylcyclohexylidenecyclohexylmethane in 130 cc. of glacial acetic acid was added 0.3 g. of platinum–oxide platinum black and the mixture was reduced by hydrogen under pressure as described by Adams and Marshall.[6] The reduction product boiled at 146–148° at 5 mm.; n_D^{20} 1.5391; d_4^{20} 0.9774; calcd. M_D, 81.96; found, M_D, 82.07.

Anal. Subs., 0.1551: CO_2, 0.5067; H_2O, 0.1570. Calcd. for $C_{19}H_{28}$: C, 88.98; H, 11.02. Found: C, 89.09; H, 11.33. Mol. wt. (cryoscopic in benzene). Subs., 0.1295: benzene, 13.1765; *At*, 0.203. Calcd. for $C_{19}H_{28}$: mol. wt., 256. Found: mol. wt., 248.

Godchot[7] has previously obtained this hydrocarbon in an impure condition by the catalytic hydrogenation of triphenylmethane over nickel.

Tetracyclohexyldiphenylethane.—The sodium derivative from 4 g. of dicyclohexylphenylchloromethane was prepared as described before and was then suspended in 50 cc. of dry, oxygen-free ether. To the cold (0°) suspension was added slowly an ether solution of tetramethylethylene bromide until the color of the metallic alkyl was no longer apparent. During the addition of this solution the reaction mixture was vigorously shaken. The mixture was filtered and the filtrate evaporated in an atmosphere of nitrogen. About 1 g. of an oil remained which could not be made to crystallize. This oil was apparently the desired hydrocarbon, as shown by the following reactions.

When about 1 g. of the oil was dissolved in 50 cc. of dry oxygen-free ether and the

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[6] Adams and Marshall, THIS JOURNAL, 50, 1970 (1928).

[7] Godchot, *Comp.* rend., 147, 1057 (1908).

mixture treated with 40 cc. of 40% sodium amalgam, the solution became red in about twenty minutes. Shaking was continued for six hours. Dry carbon dioxide was then admitted and the reaction mixture was worked up as described before for dicyclohexylphenylacetic acid. The yield of acid was 0.4 g., m. p. 242–244". A mixed melting point with the acid prepared previously showed no depression. From the same reaction mixture there was obtained 0.15 g. of the hydrocarbon $C_{38}H_{54}$ which melted at 209°.

The crude oily hydrocarbon from 4 g. of dicyclohexylphenylchloromethane was prepared and treated in dry oxygen-free ether with 110 g. of 1% sodium amalgam. The deep red color characteristic of the metallic alkyl appeared in about two and a quarter hours.

Dicyclohexylphenylmethyl Peroxide.—A slow current of dry air was bubbled through a solution of 1 g. of the freshly prepared hydrocarbon in dry ether. A white precipitate separated from the solution. This product was recrystallized from ether or from benzene and alcohol. The purified product weighed 0.5 g.; m. p. 186–188° (with decomposition).

Anal. Subs., 0.1630, 0.1297: CO_2, 0.5011, 0.3982; H_2O, 0.1479, 0.1212. Calcd. for $C_{38}H_{54}O_2$: C, 84.07; H, 10.03. Found: C, 83.86, 83.80; H, 10.03, 10.03. Mol. wt. (Rast method). Subs., 0.0109; camphor, 0.1861; *At,* 4.5" (average of 3 detns.). Calcd. for $C_{38}H_{54}O_2$: mol. wt., 542. Found: mol. wt., 521.

Three-tenths of a gram of this peroxide was slowly dissolved in 10 g. of ice-cold sulfuric acid. The reaction mixture was stirred and allowed slowly to come to room temperature. It was then poured on cracked ice and extracted with ether. The ether was evaporated and the oil was dissolved in 6 cc. of benzene and treated with 2 cc. of acetyl chloride. After standing overnight the mixture was evaporated. A few crystals were obtained which melted at 122" and showed no depression in melting point when mixed with an authentic specimen of dicyclohexylphenylchloromethane. Some unsaturated material, probably phenylcyclohexylidenecyclohexylmethane remained in the mother liquors.

Attempts to follow quantitatively the absorption of oxygen by the crude hydrocarbon were not very successful. Using oxygen-free xylene as a solvent, a preparation was made starting with 4 g. of dicyclohexylphenylchloromethane. As soon as the color of the metallic alkyl had disappeared, the apparatus was connected with a eudiometer filled with oxygen. In the first seven minutes 18 cc. of oxygen was absorbed. In the next thirty minutes 7 cc. more was absorbed. No more oxygen was absorbed in the next eight hours. On evaporating the solution and recrystallizing the residue, 0.25 g. of the peroxide was obtained. In a duplicate run 17 cc. of oxygen was absorbed in the first five minutes, 7 cc. in the next fifteen minutes and 4 cc. in the next half hour. The peroxide found amounted to 0.3 g. In a third run a weighed sample of 0.9 g. of crude ethane was used and results of the same order were obtained. In the first five minutes 15 cc. of oxygen was absorbed, in the next fifteen minutes 6 cc. and in the next hour 3 cc. The amount of oxygen absorbed would be that required for only 0.54 g. of the ethane and the peroxide isolated weighed only 0.29 g.

Stability of Tetracyclohexyldiphenylethane toward Heat and Light.—One gram of the crude freshly prepared tetracyclohexyldiphenylethane was dissolved in 60 cc. of dry oxygen-free xylene and heated to 100° for ten minutes. No color developed. The xylene was removed and the residue was recrystallized from alcohol and benzene. There was thus obtained 0.2 g. of product which by a mixed melting point determination was found to be the same hydrocarbon as that obtained as a by-product in the preparation of sodium dicylohexylphenylmethyl. In the mother liquors there was present an oily material which probably was a mixture of phenylcyclohexylidenecyclohexylmethane and phenyldicyclohexylmethane produced by disproportionation of the tetracyclohexyldiphenylethane.

When another sample of the ethane was heated for the same length of time and then shaken with 40% sodium amalgam for four hours, no red color developed, showing the absence of the starting material.

Three runs of the ethane were prepared from 4 g. of dicyclohexylphenylchloromethane. The solutions of hydrocarbon in ether were allowed to stand for different times and then treated with 40% sodium amalgam and the amount of dicyclohexylphenylacetic acid which could be isolated was noted. One sample was treated at once with amalgam and from it 0.32 g. of the acid was isolated. The second solution stood in the light for eight hours before the amalgam was added. It yielded only 0.12 g. of acid. The third solution stood in the light for five days before the amalgam was added. The amount of acid formed was too small to isolate and weigh. Several other solutions of the hydrocarbon were allowed to stand in the light and some in the dark. The hydrocarbon apparently decomposed rather rapidly in either case.

Summary

1. Dicyclohexylphenylchloromethane has been found to react with 40% sodium amalgam to give sodium dicyclohexylphenylmethyl and a hydrocarbon, $C_{38}H_{54}$.

2. Sodium dicyclohexylphenylmethyl when treated with tetramethylethylene bromide gave tetracyclohexyldiphenylethane. This hydrocarbon absorbed oxygen to give a peroxide and was cleaved by 1% sodium amalgam, indicating that it dissociated to some extent into a free radical.

3. Solutions of tetracyclohexyldiphenylethane were not colored. When the hydrocarbon was heated in solution it rearranged at least in part to the same hydrocarbon that was obtained by the action of sodium amalgam on dicyclohexylphenylchloromethane. The ethane decomposed fairly rapidly at ordinary temperatures.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

CONDENSATION OF 3-PHENYL-2,4-THIAZOLIDIONE WITH AROMATIC ALDEHYDES[1]

BY KLARE S. MARKLEY[2] AND E. EMMET REID

RECEIVED APRIL 3, 1930 PUBLISHED JULY 3, 1930

It has long been known that heterocyclic compounds containing the linkage —SCH_2CO— undergo condensation with aromatic aldehydes[3] and with substances like phthalic anhydride and nitrosodimethylaniline,[4] isatin,[5]

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[1] Presented in abstract before the Organic Division at the Columbus meeting, April, 1929.

[2] Part II of the Ph.D. dissertation of Klare S. Markley, June, 1929.

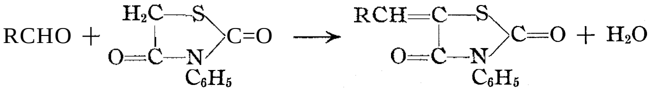
[3] Nencki, *Ber.*, **17**, 2277 (1884); Andreasch, *Monatsh.*, **8**, 407 (1887); Hann and Markley, *J. Wash. Acad. Sci.*, *16*, 169 (1926); Kingsbury and Markley, *ibid.*, **18**, *558* (1928).

[4] Kufera, *Monatsh.*, 35, 137 (1914).

[5] Andreasch, *ibid.*, **38**, 135 (1917).

alloxan[6] and phenanthraquinone.[7] The reaction conditions and the ease with which condensation occurs depend on the substituents in the heterocyclic ring and upon the nature of the oxygen-containing compound with which it reacts. Among the substances containing the above-mentioned linkage is 3-phenyl-2,4-thiazolidione, which is particularly reactive with aromatic aldehydes.

Ruhemann[8] condensed benzaldehyde, salicylaldehyde, cinnamic aldehyde and piperonal with it, employing alcohol as the solvent and piperidine as catalyst. Andreasch[9] condensed the first two of these aldehydes employing glacial acetic acid as solvent and anhydrous sodium acetate as a dehydrating agent. Since condensation occurs as a result of the splitting out of water between the methylene hydrogen of the parent substance and oxygen of the aldehyde in accordance with the equation



it is obvious that the latter method is preferable.

In view of the fact that the reaction between 3-phenyl-2,4-thiazolidione and aromatic aldehydes takes place readily and smoothly with the formation of easily isolable, stable crystalline products, a number of condensations were carried out to determine the applicability of the method for the characterization of individual members of this class of compounds.

TABLE I

3-PHENYL-2,4-THIAZOLIDIONE CONDENSATION WITH AROMATIC ALDEHYDES

Prepn.	Aldehyde Name	g.	$C_9H_7O_2NS$, g.	CH_3COOH, cc.	Time of reflux, hours	Yield of condensation product g.	%
1	p-Tolualdehyde	1.5	2.0	25	5.0	2.2	72
2	p-Hydroxybenzaldehyde	3.4	5.0	35	2.0	5.0	65
3	o-Chlorobenzaldehyde	3.7	5.0	35	2.25	5.0	61
4	Vanillin	4.0	5.0	35	2.25	5.5	65
5	Veratraldehyde	2.35	2.5	35	2.75	2.0	45
6	Piperonal	3.0	3.0	35	2.50	3.0	59
7	Furfural	3.0	4.0	60	2.0	...	
8	Anisaldehyde	3.0	4.0	35	2.25	4.0	83
9	o-Methoxybenzaldehyde	1.5	2.0	25	2.50	2.5	78
10	Benzaldehyde	2.5	4.0	30	2.0	4.0	69
11	Salicylaldehyde	2.7	5.0	30	2.25	3.5	46
12	m-Nitrobenzaldehyde	4.0	5.0	40	2.50	3.0	36
13	Cinnamic aldehyde	3.0	4.0	40	3.0	4.5	71

[a] Preparation not weighed; another preparation gave 71% yield.

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[6] Butscher, *Monatsh.*, **32,** 9 (1911).

[7] Raymond M. Hann, Master's thesis, George Washington University, 1926.

[8] Ruhemann, J. *Chem. Soc.*, 95, 117 (1909).

[9] Andreasch, *Monatsh.*, **38,** 125 and 127 (1917).

TABLE II

ANALYSES AND PHYSICAL CHARACTERISTICS OF THE ALDEHYDE CONDENSATION PRODUCTS

Prepn.	Condensation product	Physical appearance	Formula	Weight, g.	Nitrogen-K. G. A. method $N/14$ H_2SO_4 consumed, cc.	Nitrogen, % Found	Nitrogen, % Calcd.	M. p., °C.
1	5-p-Tolual-3-phenyl-2,4-thiazolidione	Pale yellow needles	$C_{17}H_{13}O_2NS$	0.3205	15.36	4.79	4.75	192
2	5-p-Hydroxybenzal-3-phenyl-2,4-thiazolidione	Short, thick lemon-yellow needles	$C_{16}H_{11}O_3NS$	.2575	12 29	4.77	4.71	257.5
3	5-*o*-Chlorobenzal-3-phenyl-2,4-thiazolidione	White, filamentous crystals	$C_{16}H_{10}O_2ClNS$	.2897	13.02	4.49	4.44	169–170
4	5-Vanillal-3-phenyl-2,4-thiazolidione	Bright yellow fragmented plates	$C_{17}H_{13}O_4NS$	.2537	11.09	4.37	4.28	234–235
5	5-Veratral-3-phenyl-2,4-thiazolidione	Long, bright yellow needles	$C_{18}H_{15}O_4NS$	.2843	11.39	4.01	4.10	208–209
6	5-Piperonal-3-phenyl-2,4-thiazolidione	Slender, bright yellow needles	$C_{17}H_{11}O_4NS$	.3407	14.52	4.26	4.31	207–208
7	5-Furfural-3-phenyl-2,4-thiazolidione	White, filamentous crystals	$C_{14}H_9O_3NS$	.2942	15.17	5.16	5.17	218–219
8	5-Anisal-3-phenyl-2,4-thiazolidione	Pale yellow, filamentous crystals	$C_{17}H_{13}O_3NS$	.2975	13 22	4 44	4 50	199–200
9	5-*o*-Methoxybenzal-3-phenyl-2,4-thiazolidione	Pale yellow microcrystalline powder	$C_{17}H_{13}O_3NS$	.2015	8.61	4.27	4.50	138–139
10	5-Benzal-3-phenyl-2,4-thiazolidione	White, microcrystalline powder	$C_{16}H_{11}O_2NS$	.2805	13.59	4.84	4.98	210–211
11	5-Salicylal-3-phenyl-2,4-thiazolidione	Brownish, yellow needles	$C_{16}H_{11}O_3NS$	.2227	10 58	4.75	4.71	235–236
12	5-*m*-Nitrobenzal-3-phenyl-2,4-thiazolidione	Pale yellow, microcrystalline powder	$C_{16}H_{10}O_4N_2S$	.2669	22.70	8.51	8.59	188
13	5-Cinnamal-3-phenyl-2,4-thiazolidione	Brilliant yellow needles	$C_{18}H_{13}O_2NS$	.2535	11.53	4.55	4.56	212–213

Results and Discussion.—Sixteen aromatic aldehydes were condensed with 3-phenyl-2,4-thiazolidione using glacial acetic acid as solvent and anhydrous sodium acetate as the dehydrating agent. Reaction occurred with the formation of well crystallized, stable products in good yield with all except resorcylaldehyde, hydrocinnamaldehyde and 2,4,6-trinitrobenzaldehyde, with which the reaction occurred to some extent but pure compounds were not isolated from the reaction mixtures. Sharp melting points were observed with most of the products although some of them partially sublimed before melting, a behavior which is also characteristic of the parent substance.

The data concerning the reaction conditions, the yield, melting point and nitrogen content of the products are recorded in Tables I and II.

Ruhemann reported the melting points of the benzylidene and salicylidene compounds at 208–209° and 238–239°, respectively, after recrystallization from alcohol; Andreasch gives 239 and 140°, respectively, whereas our compounds after recrystallization from glacial acetic acid melted at 210–211° and 235–236°, respectively.

Experimental

The parent substance, 3-phenyl-2,4-thiazolidione, was prepared by refluxing thiocarbanilide and monochloro-acetic acid for five hours in glacial acetic acid solution in accordance with the procedure described in a previous paper.[10]

The aldehyde condensations were carried out by dissolving 2 to 5 g. of 3-phenyl-2,4-thiazolidione together with slightly more than the theoretical amount of the appropriate aldehyde, in 25 to 40 cc. of glacial acetic acid containing 5 g. of anhydrous sodium acetate and heating under a reflux condenser for one and one-half to five hours. The reaction product upon cooling almost always solidified in a characteristic crystalline mass. After the addition of water, the mass was disintegrated by shaking, the fine crystalline meal thrown on a Büchner funnel, thoroughly washed with water and usually with small amounts of glacial acetic acid, 50% alcohol and again with water to insure complete removal of the sodium acetate and excess aldehyde. After drying and determining the crude yields, the compounds were recrystallized from glacial acetic acid.

The nitrogen determinations were carried out in accordance with the usual Kjeldahl–Gunning–Arnold procedure except that boric acid[11] was substituted for standard alkali for the absorption of the evolved ammonia, which was then directly titrated with $N/14$ sulfuric acid.

An electrically heated melting point apparatus and Wheeler completely immersed thermometers, standardized by the U. S. Bureau of Standards, were used in determining the melting points of the compounds. They were usually immersed at a temperature approximately 10° below the roughly determined melting point and the temperature was allowed to rise slowly to the observed melting point.

Summary and Conclusions

Thirteen aromatic aldehydes were condensed with 3-phenyl-2,4-thiazolidione and the products isolated and described. The physical appearance, melting point and nitrogen analysis of the resulting product are sufficiently distinctive to warrant the use of the method for the characterization of aromatic aldehydes.

BALTIMORE, MARYLAND.

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[10] Markley and Reid, THIS JOURNAL, 52, 2137 (1930).

[11] Markley and Hann, J. Assn. Off Agri. *Chem.*, **8**, 455 (1925)

[Contribution from the Chemical Laboratory of the University of Illinois]

THE FORMATION OF PYRROLIDINE DERIVATIVES FROM DIETHYL α,α'-DIBROMO-ADIPATE AND CERTAIN SECONDARY AMINES

By Reynold C. Fuson and Ralph A. Connor

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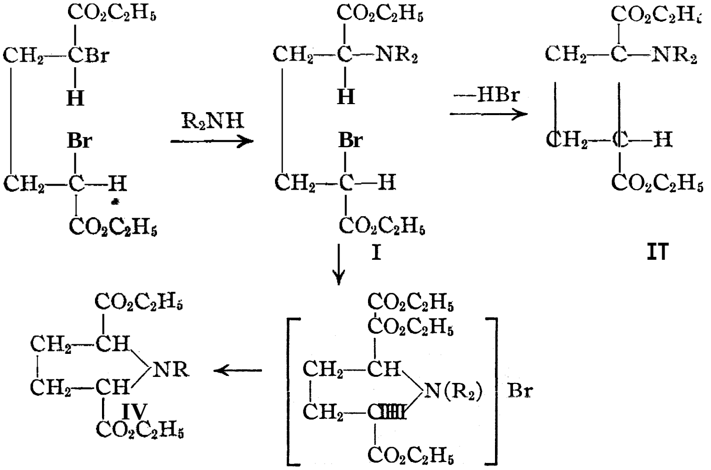
It has been shown by von Braun and his collaborators[1] that the cleavage of diethyl α,α'-dibromo-adipate by secondary amines is general for a wide variety of aliphatic amines. Of the amines whose action was studied only piperidine and dimethylamine failed to produce the cleavage. The mechanism proposed by Fuson[2] for the cleavage involves the intermediate formation of an unstable cyclobutane derivative (II) from the α-bromo-α'-dialkylamino-adipic ester (I) postulated as the initial reaction product.



This theory has been supported by evidence presented by Fuson and Kao[3] and by von Braun, Jostes and Wagner.[1] On the basis of this mechanism, there seemed to be no reason for the abnormal behavior of piperidine and dimethylamine. The action of these amines has, therefore, been reinvestigated. Work by Fuson and Bradley[4] and by von Braun[5] has subsequently shown that under favorable conditions piperidine also gives a good yield of the cleavage products.

The present paper is a report of a study of the dimethylamine case. Although it has not been possible to obtain cleavage products from α,α'-

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[1] Von Braun, Leistner and Münch, *Ber.*, 59B, 1950 (1926); von Braun, Jostes and Wagner, *ibid.*, 61B, 1423 (1928).

[2] Fuson, This Journal, 50, 1444 (1928).

[3] Fuson and Kao, *ibid.*, 51, 1536 (1929).

[4] Fuson and Bradley, *ibid.*, 51, 599 (1929).

[5] Von Braun, *Ber.*. 62B, 1694 (1929).

dibromo-adipic esters by the action of this amine, evidence has been obtained which seems to clear up the difficulty.

In studying the reaction of dimethylamine with diethyl α,α'-dibromo-adipate, the authors noted a large loss of material when the reaction mixture was worked up with dilute hydrochloric acid and ether. The aqueous solution was extracted with ether, made alkaline and again extracted with ether. The ether-soluble product so obtained amounted to less than a fourth of the starting materials. The explanation which at once suggested itself was the formation of a cyclic quaternary ammonium bromide (III, R = CH_3).

In order to test this hypothesis, the following experiments have been carried out. The reaction mixture after treatment with dilute hydrochloric acid was thoroughly extracted with benzene. The aqueous layer was then made alkaline and was again extracted repeatedly with benzene. The aqueous solution was then distilled under diminished pressure. After the water had been distilled the residue was heated until decomposition took place. In this way, there was obtained a water-insoluble base which has been shown to be diethyl 1-methyl-pyrrolidine-2,5-dicarboxylate.

The identity of the diethyl 1-methyl-pyrrolidine-2,5-dicarboxylate was established by a comparison of its chloroplatinate with that of an authentic specimen made by the method of von Braun and Seemann.[6] The melting point of a mixture of the two chloroplatinates showed no depression.

Results very similar to these have been reported by Le Sueur and Haas[7] who obtained dialkyl 1-phenylpyrrolidine-2,5-dicarboxylates by treating α,α'-dibromo-adipic esters with mono- and diethylaniline. It would appear from the present work that, in these cases, also, a cyclic quaternary ammonium bromide (III) is formed as an intermediate product which yields the pyrrolidine derivative (IV) when decomposed by heat.

Experimental Part

Meso-diethyl α,α'-Dibromo-adipate and Dimethylamine.—To 108 g. of a 25% solution of dimethylamine in absolute alcohol (0.6 mole of dimethylamine) was added 36 g. (0.1 mole) of meso-diethyl α,α'-dibromo-adipate. The mixture was heated gently to bring the ester into solution, and after a few minutes reaction was evidenced by the evolution of heat which soon caused the solution to boil. After two hours' refluxing on the steam-bath, the clear slightly yellow solution was placed in a Claisen flask and the alcohol and excess amine distilled under diminished pressure (water pump).

The residue, which consisted of a mixture of crystals and a viscous liquid, was filtered, the crystals were washed thoroughly with dry benzene and the latter was then used to extract any benzene-soluble material from the filtrate. The benzene solution was dried over sodium sulfate and distilled. It yielded 3 g. of an oil boiling at 140–145° (8 mm.), 150–160° (20 mm.). This corresponds to the diethyl or,&'-tetra-ethyl-diamino-adipate $(CH_2CHN(CH_3)_2CO_2C_2H_5)_2$ described by von Braun and Munch and represents a yield of 20% of the theoretical.

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[6] Von Braun and Seemann, *Ber.*, **56B**, 1841 (1923).

[7] Le Sueur and Haas, *J. Chem. Soc.*, 97, 173 (1910).

The water-soluble, benzene-insoluble portion of the residue after being, as indicated above, repeatedly washed with benzene, was placed in a Claisen flask and heated under diminished pressure. The temperature of the bath was gradually raised to about 250°. An oily distillate was obtained, part of which crystallized at once and proved to be dimethylamine hydrobromide. The oil was washed with water, dried over potassium carbonate and distilled. There was obtained 2 g. of a slightly yellow oil boiling at 112–113° (3 mm.). The chloroplatinate formed in deep yellow crystals melting at 180–180.5° (corr.).

The chloroplatinate of the base was prepared by dissolving 0.2 g. in 2 cc. of 95% alcohol and 1 cc. of dilute hydrochloric acid, and adding to this solution 4.5 g. of a 10% solution of chloroplatinic acid. The solution was concentrated on a steam-bath and allowed to stand overnight at 0°. Deep yellow crystals were obtained which after repeated recrystallization from alcohol melted at 180–180.5° (corr.). It was found that the precipitation of the chloroplatinate from the reaction mixture could be induced by the addition of a little ether. A mixture of the chloroplatinate with that of diethyl 1-methylpyrrolidine-2,5-dicarboxylate, prepared as described below, melted at 179–180° (corr.).

The Chloroplatinate of Diethyl 1-Methylpyrrolidine-2,5-dicarboxylate.—This salt was prepared by the method of von Braun and Seeman. From 36 g. of diethyl α,α'-dibromo-adipate and 310 g. of a 30% solution of methylamine in absolute alcohol (corresponding to 0.3 mole of methylamine) 2 g. or 10% of the theoretically possible yield, of diethyl 1-methylpyrrolidine-2,5-dicarboxylate was obtained. The chloroplatinate melted at 179–180° (corr.).

Summary

The failure of dimethylamine to bring about the dibromo-adipic ester cleavage is accounted for by the fact that the chief reaction in this case is one leading to the formation of a water-soluble, benzene-insoluble product which is believed to be the cyclic quaternary ammonium bromide. This explanation is supported by the fact that the material when dry distilled yields diethyl 1-methyl-pyrrolidine-2,5-dicarboxylate.

The formation of dialkyl 1-phenylpyrrolidine-2,5-dicarboxylates when mono- or diethylaniline is used is explained by a similar mechanism.

URBANA, ILLINOIS

[CONTRIBUTION NO. 60 FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

SCISSION OF THE METHYLENEDIOXYL GROUP WITH ALUMINUM BROMIDE[1]

BY ERICH MOSETTIG AND ALFRED BURGER

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The conversion of methylene ethers into the corresponding dihydroxy derivatives has been for many years a process of considerable importance, because of the frequent occurrence of this grouping in natural products, particularly among the alkaloids. By scission of the methylenedioxyl ring the parent dihydroxy compounds, as well as the monomethyl and dimethyl ethers, are made accessible.

The opening of this ring has for the most part been accomplished through the action of concentrated acid or alkali at elevated temperatures.[2] In recent years, Spath and his co-workers have systematically investigated the method, first devised by Tollens, Weber and Clowes[3] for quantitative estimation of the methylenedioxyl group, which depends upon the immediate destruction of the formaldehyde with phenolic substances. This was elaborated for preparative purposes, and employed with great success in alkaloid chemistry.[4] Phosphorus pentachloride has been employed by Fittig and Remsen,[5] R. Wegscheider,[6] and A. Pauly.[7] Most recently, Parijs[8] has used absolute nitric acid and acetic anhydride to split methylene ethers.

Aluminum halides, especially the chloride, have found much use in the laboratory and in industry in the scission of ethers and have been successfully applied to a number of alkaloids.[9] Aluminum bromide compounds with aromatic ethers were first described by Kohler;[10] they have recently been studied exhaustively by Pfeiffer,[11] who proposed a mechanism for the demethylation process. The splitting of the methylenedioxyl group with aluminum chloride has been attempted only in isolated cases,[12] in which

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[1] This investigation was supported by the Committee on Drug Addiction of the National Research Council.

[2] A complete bibliography on the subject is given in the paper of Spath and Quietensky, *Ber.*, 60, 1882 (1927).

[3] Tollens, Weber and Clowes, *Ann.*, 299, 316 (1898); *Ber.*, 32, 2841 (1899).

[4] Späth and Quietensky, *ibid.*, 58, 2267 (1925); Spnth and Holter, *ibid.*, 60, 1891 (1927); Spath and Mosettig, *ibid.*, 59, 1496 (1926).

[5] Fittig and Remsen, *Ann.*, 159, 144 (1871).

[6] Wegscheider, *Monatsh.*, 14, 382 (1893).

[7] Pauly, *Ber.*, 40, 3096 (1907).

[8] Parijs, *Rec. trav. chim.*, **49**, 33 (1930).

[9] Oberlin, *Arch. Pharm.*, 265, 256–273 (1927).

[10] Kohler, *Am. Chem. J.*, 27, 249 (1902).

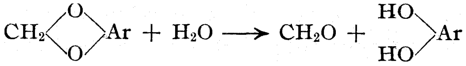
[11] Pfeiffer, *Ann.*, 460, 156 (1928).

[12] Dreyfus, German Patent 193,958; Thoms and Biltz, *Arch. Pharm.*, 242, 87 (1904); Mauthner, *J. prakt. Chem.*, [2] *119*, 74 (1928); see also Ref. 9.

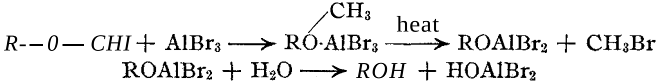
the conditions (especially temperature) are such that the method has a very limited field of application.

The more active and more soluble aluminum bromide would be expected to accomplish the desired result under milder experimental conditions. We have in fact found it possible to carry out the reaction with a number of methylene ethers at room temperature or even at 0°, with very satisfactory yields. The most suitable solvent proved to be nitrobenzene, because of its ability to dissolve the reacting substances and to hold the resulting aluminum bromide double compound in solution.

It seems quite certain that the scission with acids takes place according to the equation

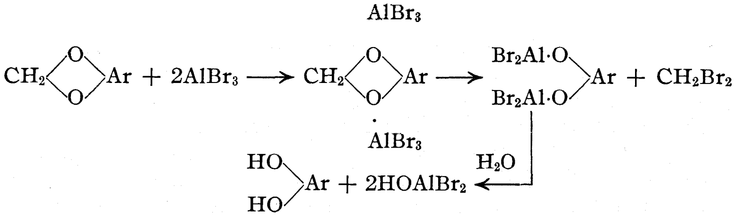


but to our knowledge no mechanism has been proposed for the action of the aluminum halides. According to Pfeiffer,[11] the demethylation process takes the following course



$$R\text{--}0\text{—}CHI + AlBr_3 \longrightarrow \overset{CH_3}{RO}\cdot AlBr_3 \xrightarrow{\text{heat}} ROAlBr_2 + CH_3Br$$
$$ROAlBr_2 + H_2O \longrightarrow ROH + HOAlBr_2$$

and it is not unreasonable to assume that in the case of methylene ethers a similar mechanism is applicable



In support of this assumption, we find that at least two molecules of aluminum bromide must be used for each molecule of methylene ether. With piperonal, for example, the yield of protocatechuic aldehyde was halved when but one molecule of aluminum bromide was used. Similarly, the reaction runs most favorably with acetopiperone in the presence of three molecules of aluminum bromide, in accordance with the Pfeiffer[11] theory that the carbonyl group also adds a molecule of aluminum halide. Since we were interested primarily in the perfection of a preparative method, further quantitative investigations to determine the course of the reaction were not undertaken.

The methylene ethers chosen for investigation were: piperonal, piperonylic acid and its methyl ester, acetopiperone, m-nitrocatechol methylene ether, 2,3-methylenedioxy-phenanthrene-9-carboxylic acid, and inactive tetrahydroberberine. It is rather remarkable that, under conditions which give smooth scission of the methylene ether group, the methoxyl group is scarcely affected. In parallel experiments with veratric aldehyde, only traces of alkali-soluble material were obtained; in the case of tetrahydroberberine, the two methoxyl groups remained intact. The ester group in piperonylic acid methyl ester was hydrolyzed only to a small extent.

The method is not applicable to those substances which are extremely sensitive toward aluminum bromide or which may undergo reaction with the methylene bromide assumed to be among the products. It was not possible, for example, with safrole, isosafrole or piperonyl alcohol (even after benzoylation of the alcoholic hydroxyl) to isolate the expected dihydroxy compounds. Instead of these, sparingly soluble, alkali-insoluble amorphous substances were obtained, which probably represented condensation products. The reaction likewise failed with 2,3-methylenedioxy-phenanthrene. 2,3-Methylenedioxy-phenanthrene-9-carboxylic acid, on the other hand, was converted in nearly quantitative yield to 2,3-dihydroxy-phenanthrene-9-carboxylicacid, which could then be decarboxylated to the desired 2,3-dihydroxy-phenanthrene.

In contrast to the methylenedioxyl group, the ethylenedioxyl group is exceedingly stable, and even at temperatures up to 130° no ring-opening took place with pyrocatechol ethylene ether, or pyrocatechuic acid ethylene ether.

Experimental Part

The aluminum bromide employed in the following investigations was distilled from aluminum chips before each experiment. The nitrobenzene was dried over calcium chloride. All high-vacuum sublimations were carried out in pyrex bulb-tubes sealed directly onto an efficient mercury-vapor pump.

Preparation of Protocatechuic Aldehyde from **Piperonal.**—Five grams of piperonal was dissolved in 15 cc. of nitrobenzene and cooled to about 10°. To this was added a cold solution of 18 g. of aluminum bromide (about 2 mols) in 20 cc. of nitrobenzene, giving a deep red solution. After five hours' standing at room temperature, the reaction mixture was poured into 300 cc. of water containing a small amount of hydrochloric acid. The aqueous layer, separated from the nitrobenzene, was extracted with ether. The combined ether extract and nitrobenzene was washed with a little water and the protocatechuic aldehyde extracted with dilute sodium hydroxide. This alkaline solution was extracted with ether to remove traces of nitrobenzene, acidified, saturated with salt and extracted exhaustively with ether. The ether solution, dried with sodium sulfate, yielded on distillation an oil which soon crystallized. After recrystallization from 500 cc. of boiling toluene, the substance melted at 151–153°. Sublimation in high vacuum yielded long white needles of m. p. 154–155.5°. It was readily soluble in alkali and its aqueous solution gave with ferric chloride the characteristic green color of protocatechuic aldehyde. The yield was **3.8** g., 82% of the calculated.

Another experiment carried out under the same conditions was interrupted at the end of fifteen minutes and worked up as described. Even after this short reaction period, the yield amounted to 56% of the theoretical.

If piperonal and aluminum bromide are allowed to react in equimolecular amounts for eleven hours, a yield of 41% of protocatechuic aldehyde is obtained, and about 40% of the piperonal used can be regained with sodium bisulfite.

To compare the action of aluminum bromide on the methoxyl group, veratric aldehyde was treated with aluminum bromide under the conditions described above. Alkali-soluble substances were obtained only in traces; judging from odor, these may have been vanillin or isovanillin. No protocatechuic aldehyde was formed (negative ferric chloride test).

Preparation of Protocatechuic Acid from Piperonylic Acid.—Nine grams of finely powdered piperonylic acid suspended in 180 cc. of nitrobenzene was treated with a solution of 3 g. of aluminum bromide in 70 cc. of nitrobenzene, whereby the piperonylic acid went into solution. The red solution stood for four hours at room temperature and was then poured into 400 cc. of acidified ice water. The nitrobenzene was distilled off with steam and the aqueous solution concentrated to 200 cc. Most of the protocatechuic acid separated crystalline at this point. The remainder was obtained by ether extraction of the mother liquors from the crystallization. After treatment with animal charcoal in 30 cc. of boiling water, the acid was obtained nearly pure in a yield of 7.7 g., 92% of the theoretical. Purified by high-vacuum sublimation, it had the m. p. 200–202°.

Protocatechuic Acid Methyl Ester from Piperonylic Acid Methyl Ester.—Piperonylic acid methyl ester was prepared by heating 2 g. of piperonylic acid in 80 cc. of methyl alcohol with 2 g. of concd. sulfuric acid After neutralization of the sulfuric acid the alcohol was distilled off in a strong current of carbon dioxide and the residue dissolved in ether, which was now washed with dilute soda solution and dried over sodium sulfate. The oily residue from distillation of the ether was distilled in a vacuum (12 mm.). The highly refracting distillate solidified on cooling, m. p. 49.5–50.5°, yield 2 g.

A solution of 2.6 g. of the methyl ester in 52 cc. of nitrobenzene was cooled in ice and treated with a cold solution of 8 g. of aluminum bromide in 35 cc. of nitrobenzene. After three and one-half hours at room temperature the mixture was poured into ice water, acidified, extracted with ether and the ether–nitrobenzene solution extracted as rapidly as possible with very dilute ice-cold sodium hydroxide. The alkaline solution was made weakly acid immediately, saturated with salt, and extracted exhaustively with ether; 0.2 g. of protocatechuic acid was removed from the ether by shaking with dilute sodium bicarbonate. Distillation of the ether yielded an oily product, which solidified to faintly colored crystals on standing in a vacuum desiccator overnight. The melting point was 130–133°, unsharp; the yield, 1.43 g. or 58% of the theoretical amount. After high-vacuum sublimation it was obtained in radiated clusters of crystals, m. p. 134.5–135°.[13]

3,4-Dihydroxyacetophenone from Acetopiperone.—One gram of acetopiperone[14] dissolved in 10 cc. of nitrobenzene was treated with a solution of 5.3 g. (somewhat more than 3 mols) of aluminum bromide in 40 cc. of nitrobenzene. After two and one-half hours' reaction at room temperature, the mixture was poured into acidified ice water, the nitrobenzene layer diluted with ether, separated, and the phenolic product shaken into 0.5 *N* potassium hydroxide. This was acidified and exhaustively extracted with ether. The product, which separated nearly pure, was further purified by cautious precipitation from its xylene soiution with petroleum ether, or by high-vacuum sublimation. The pure substance melted at 117–118°;[15] yield, 0.45 g, 48% of the theoretical amount.

4-Nitropyrocatechol from 4-Nitropyrocatechol Methylene Ether.—The methylene ether used was obtained as a secondary product from the nitration of piperonal by the

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[13] Matsmoto, Ber., 11, 129 (1878), gives the m. p. 134.5".

[14] Prepared by the method of Mosettig and Jovanovič, *Monatsh.*, 53 and 54, 427 (1929).

[15] Mauthner, *J. prakt. Chem.*, [2] 119, 74 (1928); Dzierzgowski, *Ber.*, **27,** 1988 (1894), give the m. p. 116°.

method of Ekeley and Klemme.[16] Five grams of 4-nitropyrocatechol methyiene erher in 70 cc. of nitrobenzene was treated with a cold solution of 18 g. of aluminum bromide in 60 cc. of nitrobenzene with good cooling and allowed to react for one and one-half hours at 0°. At the end of this time the double compound had precipitated in part from the solution. The mixture was decomposed with ice-cold dilute hydrochloric acid and the phenolic products extracted from the nitrobenzene layer with alkali. When the purple alkaline solution was acidified, a nearly insoluble substance precipitated and was filtered off. This material was not further investigated. The filtrate was concentrated and the 4-nitropyrocatechol extracted with ether. Crystallization from water gave 3 g. of pure substance, corresponding to 65% yield. It sublimed readily in a vacuum, m. p. 174–175°, agreeing with the melting point given in the literature.[17]

Scission of the Methylene Ether Group of Inactive **Tetrahydroberberine.[18]—Five** grams of tetrahydroberberine in 150 cc. of nitrobenzene was cooled to a point just above that where the nitrobenzene started to crystallize and a cold solution of 8.5 g. of aluminum bromide in 85 cc. of nitrobenzene added slowly, cooling in a freezing mixture. After standing for one-half hour at this temperature with frequent shaking, the reaction mixture was poured into 500 cc. of ice water containing 20 cc. of hydrobromic acid. A heavy precipitate of hydrobromides separated, which was filtered out and washed with ether. The filtrate was freed from nitrobenzene by extracting with ether and the bases remaining in it were thrown out as hydriodides with a large excess of potassium iodide. These salts were dissolved in water together and the solution made alkaline. By shaking out with ether, about 30% of the tetrahydroberberine employed was regained. The red alkaline solution was acidified, again made alkaline with sodium bicarbonate, and the dihydroxy base extracted into a large amount of ether. Concentration of the ether to about 100 cc. yielded the base in colorless micro crystals; 3 g. of product was obtained, melting in a vacuum at 260–261°. The substance agreed also in its other properties with the base described by Spath and Mosettig.[4]

Anal. Subs., 6.573 mg.: AgI, 9.118 mg. (Zeisel–Pregl). Calcd. for $C_{17}H_{13}(OH)_2(OCH_3)_2N$: OCH_3, 18.97. Found: OCH_3, 18.33.

For further confirmation, our dihydroxy base was methylated with diazomethane[4] and racemic tetrahydropalmatine (m. p. 147–148°) obtained.

Synthesis of 2,3-Dihydroxy-phenanthrene.—This preparation was carried out according to the Pschorr method for the synthesis of phenanthrene derivatives.

The 6-nitropiperonal was prepared and purified by the method of Ekeley and Klemme.[16]

α-Phenyl-2-nitro-4,5-methylenedioxy-cinnamic Acid.—Twenty grams of 6-nitropiperonal was heated with 15.2 g. of anhydrous sodium phenylacetate and 1 g. of anhydrous zinc chloride in 85 cc. of acetic anhydride for four and one-half hours in an oil-bath at 110–120°. The reaction mixture was poured into 500 cc. of water and, after the initial cloudiness had settled, the clear solution was decanted from the brown resinous products. These resins were brought into solution by boiling with 3 liters of water, with addition of concd. ammonia, and filtered through a layer of paper pulp. The filtrate was acidified and the pale yellow precipitate of acid filtered out. It was dried and recrystallized from about 60 parts of boiling benzene. The yield was 17.3 g., 54% of the theoretical. It consisted of pale yellow crystals, m. p. 193–195°.

Anal. Subs., 7.185 mg.: N, 0.305 cc. (25°, 740 mm.). Calcd. for $C_{16}H_{11}O_6N$: N, 4.47. Found: N. 4.73.

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[16] Ekeley and Klemme, THIS JOURNAL, 50, 2711 (1928).

[17] Kempf, *J. prakt. Chem.*, [2] 78, 257 (1908); Dakin, *Am. Chem. J.*, 42, 490 (1909).

[18] Spath and Mosettig (Ref. 4) accomplished this with phloroglucinol and sulfuric acid at 100°.

α-Phenyl-2-amino-4,5-methylenedioxy-cinnamic Acid.—Five grams of the nitro acid was dissolved in 30 cc. of water and 10 cc. of 25% ammonia, heated to boiling and poured into a suspension of ferrous hydroxide, prepared from 35 g. of hydrated ferrous sulfate in 105 cc. of water with 20 cc. of 25% ammonia. This was heated for one-half hour on the steam-bath with frequent shaking and filtered through paper pulp. The pulp filter and residue was boiled out three times with dilute ammonia and the combined ammoniacal liquors acidified with acetic acid. The amino acid, which separated in yellow crystals, was filtered out and dried at 100°. The yield was 2.8 g., 62% of the theoretical. After recrystallizing from boiling toluene it melted at 201–203" (decomp.).

If the ammoniacal solution is acidified with hydrochloric instead of acetic acid, the amino acid separates in pale pink crystals, which become yellow on drying at 100°. The acid apparently exists in two modifications, as other authors[19] have shown with analogous compounds.

Anal. Subs., 7.050 mg.: N, 0.328 cc. (27°, 747 mm.). Calcd. for $C_{16}H_{13}O_4N$: N, 4.95. Found: N, 5.20.

2,3-Methylenedioxy-phenanthrene-9-carboxylic Acid.—Ten grams of the amino acid, suspended in 200 cc. of water, was neutralized with a solution of 2.8 g. of sodium carbonate and mixed with 44 cc. of normal sodium nitrite solution. The mixture was now added dropwise with mechanical stirring to 140 cc. of ice-cold 5 N sulfuric acid keeping the temperature below 2°. At the end of the reaction, the solution was filtered, molecular copper[20] added and the suspension stirred for one hour at 75°. After cooling the precipitate of copper and phenanthrene-carboxylic acid was filtered off, the acid dissolved out by hot ammonia and reprecipitated with hydrochloric acid. Recrystallized from boiling xylene, it melted at 259–260°. It consists of colorless crystals, which sublime in high vacuum.

Anal. Subs., 0.0980: CO_2, 0 2595; H_2O, 0.0359. Calcd. for $C_{16}H_{10}O_4$: C, 72.16; H, 3.80. Found: C, 72.22; H, 4.10.

The methyl ester was prepared by refluxing a suspension of the acid in absolute methyl alcohol containing 5% of concd. sulfuric acid. The organic acid dissolved completely after about forty-five minutes and the reaction was stopped at the end of four hours. The sulfuric acid was neutralized with potassium hydroxide arid the mixture poured into ten times its volume of water. The amorphous precipitate soon crystallized and was filtered off and washed with dilute sodium carbonate. Recrystallization from methyl alcohol gave white needles in a yield of 76%; m. p. 151–151.5°.

Anal. Subs, 0.1370: CO_2, 0.3666; H_2O, 0.0562. Calcd. for $C_{17}H_{12}O_4$: C, 72.83; H, 4.32. Found: C, 72.98; H, 4.59.

2,3-Dihydroxy-phenanthrene-9-carboxylic Acid.—Two grams of finely powdered methylenedioxy-phenanthrene-carboxylic acid was suspended in 20 cc. of nitrobenzene and treated with 3.5 g. of aluminum bromide in 30 cc. of nitrobenzene. The acid went into solution with deep red color. After three hours at room temperature it was poured into ice-cold diluted sulfuric acid. The larger part of the dihydroxy product separated and was filtered off and pressed dry. A little more was obtained from extraction of the nitrobenzene layer with sodium hydroxide. The acid was purified by dissolving in sodium hydroxide, filtering and precipitating with acids. The crude product was obtained in a yield of about 97%. The acid starts to decompose at about 280°; its solution in dilute alcohol gives a deep blue color with ferric chloride. Since no suitable solvent could be found for recrystallizing the acid, the crude substance was used for decarboxylation.

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[19] Pschorr, *Ber.*, **39,** 3110 (1906); **29,** 499 (1896); Mayer and Balle, *Ann.*, 403, 194 (1914).

[20] Gattermann, *Ber.*, **23,** 1219 (1890).

2,3-Dihydroxy-phenanthrene.—One gram of crude dihydroxy-phenanthrene-carboxylic acid was distilled at 25–30 mm. pressure in a hard-glass bulb-tube. The distillate was dissolved in ether and washed with dilute sodium bicarbonate to remove unchanged acid. The dihydroxy-phenanthrene was extracted from the ether with dilute alkali, precipitated with acid and again brought into ether. Distillation of the ether gave a fairly pure, crystalline product in 46% yield. The substance is quite soluble in most organic solvents, excepting benzene, insoluble in water or petroleum ether. The best purification method is high-vacuum distillation or sublimation and recrystallization from benzene; m. p. 158.5–159°.

Anal. Subs., 0.1005: CO_2, 0.2942; H_2O, 0.0446. Calcd. for $C_{14}H_{10}O_2$: C, 79.97; H, 4.80. Found: C, 79.84; H, 4.97.

The dihydroxy-phenanthrene was converted to its dimethyl ether, previously prepared by Pschorr in another way: 0.3 g. of dihydroxy-phenanthrene was dissolved in 1 cc. of absolute methyl alcohol and the ethereal diazomethane solution from 1 cc. of nitrosomethylurethan added. After ten hours the mixture was washed with dilute alkali and the ether distilled off. The residue was recrystallized from methyl alcohol and sublimed in high vacuum; m. p. 130.5–132° (Pschorr, m. p. 131°). The picrate showed the melting point 126.5–127.5°, given by Pschorr.[21]

2,3-Methylenedioxy-phenanthrene.—One gram of 2,3-methylenedioxy-phenanthrene-carboxylic acid was distilled slowly at 250 mm. pressure. The distillate was taken up in ether and washed with dilute potassium hydroxide. The residue obtained from distillation of the ether, recrystallized from methyl alcohol, had the m. p. 93–94". The yield varies from 45 to 50%.

Anal. Subs, 0.0973: CO_2, 0 2899; H_2O, 0 0404. Calcd. for $C_{15}H_{10}O_2$: C, 81 05; H, 4.54. Found: C, 81.26; H, 4.65.

The brick-red picrate, recrystallized from methyl alcohol, melts at 151–152°.

Anal. Subs., 5.764 *mg.:* N, 0.481 cc. (25°, 740 mm.). Calcd. for $C_{21}H_{13}O_9N_3$: N, 9.32. Found: N, 9.31.

The ring-opening of tnethylenedioxy-phenanthrene was unsuccessful. We obtained only amorphous, brown-colored substances, sparingly soluble in water or ether, soluble with difficulty in alkali.

Summary

A new method of converting methylene ethers to the corresponding dihydroxy compounds is described. The reaction offers special advantages in operating at temperatures from 0 to 20°, and leaving methoxyl or ester groupings practically intact.

It has been employed successfully with the methylene ethers of a variety of aromatic compounds, and with one alkaloid.

The preparation of 2,3-dihydroxy-phenanthrene and its methylene ether is described.

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[21] Pschorr, *Ber.*, **33,** 1829 (1900).

THE ACTION OF HYDROGEN PHOSPHIDE ON FORMALDEHYDE, II[1]

BY ALFRED HOFFMAN

RECEIVED APRIL 9, 1930 PUBLISHED JULY 3, 1930

As a preface to the second communication on this subject, it may be of interest to state briefly why this investigation was undertaken. As the result of investigations in various branches of science, a number of authors have expressed the opinion in recent years that the original atmosphere of the earth contained little free oxygen. It has seemed not unreasonable, to the present writer, to go a step further and to consider some of the reactions that might have taken place if free oxygen were absent altogether. Under those conditions complex compounds might have been formed, which would constitute a starting-point for further organic evolution. Without going into the various cosmogonic theories, it may be said that such an atmosphere, similar to the sun's, would contain free hydrogen and carbon monoxide and dioxide, which react to give formaldehyde under certain conditions,[2] and hydrogen chloride, which would generate hydrogen phosphide from phosphides present in the original crust (meteorites usually contain phosphides). On the other hand, compounds of phosphorus with formaldehyde (which has a genetic relation to the sugars) would seem to be of interest in view of the groupings occurring in the nucleic acids, the distinctive components of the most vital part of the cell.

In the first article the primary condensation product $(CH_2OH)_4PCl$ was described and referred to as tetrahydroxymethylene-phosphonium chloride in analogy to the term tetrahydroxyethylidene-phosphine for $(CH_3CH\text{-}OH)_3P(C(OH)CH_3)$ as used in Beilstein.[3] As the constitution of the compound is now fully established, it will conform better to modern nomenclature to call it tetrakis(hydroxymethyl)phosphonium chloride.

Continuing the former work, a more detailed investigation of the action of alkalies and of carbonates on the mother substance was undertaken. This action was found to take place in two steps. Using sodium hydroxide at room temperature or with gentle heating not above 80°, one molecule of hydrogen is evolved and the action stops with the formation of tris(hydroxymethyl)phosphine oxide. On boiling, a second molecule of hydrogen is given off. An alkaline carbonate, such as sodium carbonate, gives the same results, but the action is slower. A neutral carbonate, like calcium or barium carbonate, produces but one molecule of hydrogen, even on long boiling. Subsequent addition of sodium hydroxide to the boiling solution frees the second molecule of hydrogen.

The intermediate compound, tris(hydroxymethyl)phosphine oxide, may

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[1] Alfred Hoffman, THIS JOURNAL, 43, 1684 (1921).

[2] Beilstein, 4th ed., Vol. I, p. 559.

[3] Beilstein, 3d ed., Vol. I, p. 921.

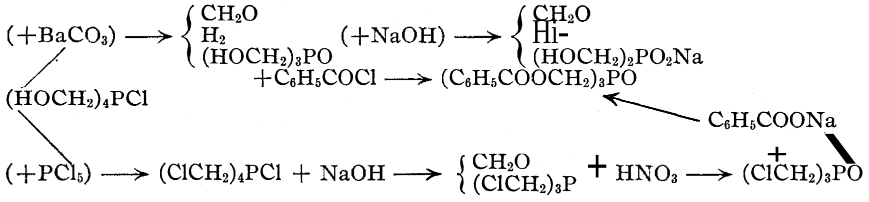
be isolated as a sirup or as its crystalline tribenzoate. Either of these compounds evolves a molecule of hydrogen on boiling with sodium hydroxide. The final product of the reaction is bis(hydroxymethyl)phosphinic acid, $(HOCH_2)_2PO_2H$, which was isolated as a crystalline barium salt.

As a test for the presence of hydroxyl groups, the action of phosphorus pentachloride on the mother substance was investigated. A well-crystallizing substance, tetrakis(chloromethyl)phosphonium chloride, $(CH_2Cl)_4PCl$, was obtained. The solution of the chloride reacts with alkalies, ammonia or even sodium bicarbonate to give the oily tris(chloromethyl)phosphine, according to the reaction

$$(ClCH_2)_4PCl + 2NaOH = (ClCH_2)_3P + CH_2O + 2NaCl + H_2O$$

The ready hydrolyzation of the tetrakis(chloromethyl)phosphonium chloride seems to indicate that the corresponding hydroxide is a feeble base. Tris(chloromethyl)phosphine also has but slight basic properties. It is soluble in strong mineral acids, but the solution hydrolyzes completely on evaporation. Dry hydrogen chloride passed into the carbon bisulfide solution of the phosphine did not seem to react. Unlike trimethylphosphine,[4] the trichloroderivative shows no tendency to oxidize to the corresponding oxide by exposure to the air, but by boiling with nitric acid the crystalline tris(chloromethyl)phosphine oxide was obtained. On heating the trichloro oxide with dry sodium benzoate to 200°, the tribenzoate of tris(hydroxymethyl)phosphine oxide was formed, identical with the product of the action of benzoyl chloride on the latter. An attempt was made to prepare the oxide by the action of phosphorus pentachloride on tris(hydroxymethyl)phosphine oxide, but only black, tarry products were obtained.

The flow sheet illustrates the relation of the compounds described.



Experimental Part

Analysis of the Tribenzoate of Tris(hydroxymethyl)phosphine Oxide.—In the first article the composition of this substance was given tentatively as $C_{24}H_{21}O_8P$, as based on the phosphorus content. The carbon determination by combustion gives widely varying results due to the occlusion of carbon by phosphoric acid or phosphates. It has now been found possible to obtain good results by wet oxidation using chromic acid.[5] This showed that the true composition is $C_{24}H_{21}O_7P$. The hydrogen was determined by the usual combustion.

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[4] Cahours and A. W. Hofmann, *Ann.*, 104, **30** (1857).

[5] Messinger, *Ber.*, **23**, 2757 (1892).

Anal. Calcd. for $C_{24}H_{21}O_7P$: C, 63.72; H, 4.6; P, 6.8. Calcd. for $C_{24}H_{21}O_8P$: C, 61.5; H, 4.4; P, 6.6. Found: C, 63.48, 63.61; H, 4.8; P, 6.9.

Action of Barium Carbonate and of Sodium Hydroxide on Tetrakis(hydroxymethyl)-phosphonium Chloride.—0 2148 g. of the chloride in 5 cc. of water was boiled with barium carbonate for eight hours; 24.9 cc. of hydrogen was given off, when all action ceased. Calcd. for $1H_2$: 29.6 cc. Then a solution of sodium hydroxide was added and on boiling an additional 29 cc. of hydrogen was obtained.

Action of Sodium Hydroxide on Tri(hydroxymethyl)phosphine Oxide Tribenzoate.—1.0338 g. of tribenzoate boiled with 1 g. of sodium hydroxide in 8 cc. of water gave 54.5 cc. of hydrogen; calcd. for $1H_2$ under the same conditions: 55 4 cc.

Preparation of Tetrakis(chloromethyl)phosphonium Chloride.—Six and six-tenths grams of tetrakis(hydroxymethyl)phosphonium chloride and 30 g. of phosphorus pentachloride in 100 cc. of carbon tetrachloride were boiled gently for four hours. Hydrogen chloride was evolved and the product separated in crusts. These were filtered with suction, washed with a little carbon tetrachloride and recrystallized from a mixture of 80 cc. of ethyl acetate and 15 cc. of methyl alcohol; yield 7.7 g.; calcd., 9.2. g. The product consists of white crystals, easily soluble in water, but not hygroscopic. It is easily soluble in methyl and ethyl alcohols, difficultly in ethyl acetate, chloroform and carbon tetrachloride. The dry compound is odorless, but its aqueous solution has a distinct odor due to hydrolysis and the breaking up of the phosphonium hydroxide into the phosphine. It melts at 192–193°.

Anal. Calcd. for $C_4H_8Cl_5P$: Cl, 67.1; P, 11.7. Found: Cl, 66.7; P, 11.2.

If the substance is dissolved in water, acidified with nitric acid and silver nitrate added, one molecule of silver chloride is precipitated; calcd. for 1 Cl, 13.4; found, 13.3. If, however, the aqueous solution is treated with sodium bicarbonate and, after removing the phosphine with carbon bisulfide, treated with nitric acid and silver nitrate, two molecules of silver chloride are formed: calcd. for 2 Cl, 26.8; found, 26.34. If the solution is treated with sodium hydroxide and let stand for a week or more, the phosphine again dissolves and the chlorine is practically all in the ionized form: calcd. for 4 Cl, 53.6; for 5 Cl, 67.1; found, Cl, 56.2.

Preparation of Tris(chloromethyl)phosphine.—Five grams of tetrakis(chloromethyl)-phosphonium chloride in 20 cc. of water was treated with 8 g. of sodium bicarbonate. The solution became milky and gave a strong formaldehyde reaction with fuchsin reagent. The phosphine was shaken out with carbon bisulfide, dried over sodium sulfate and distilled under diminished pressure; b. p. 100° (7 mm.). Heated at atmospheric pressure it decomposes. It is a colorless, mobile liquid of a powerful, benumbing odor; sp. gr. 20°, 1.414. It appears to be stable indefinitely in contact with air, showing no signs of oxidation. It is slightly soluble in water and easily in organic solvents.

Anal. Calcd. for $C_3H_6Cl_3P$: Cl, 59.3. Found: Cl, 59.4.

Preparation of Tris(chloromethyl)phosphine Oxide.—0.75 g. of the phosphine was boiled for one hour with 4 cc. of nitric acid (sp. gr. 1.2). After evaporating on the water-bath until the odor of nitric acid had disappeared, a sirup remained which crystallized on cooling; m. p. 88–89°; easily soluble in water and alcohol. For analysis it was dried *in vacuo* at 78°.

Anal. Calcd. for $C_3H_6OCl_3P\cdot{}^1/_2HO$: Cl, 52.1. Found: Cl, 52.2, 52.23.

Mixed with sodium benzoate and heated at 200° for one hour, a waxy material resulted. After removing the excess sodium benzoate with boiling water, an oil remained which solidified on cooling. Recrystallized from methyl alcohol, it melted at 110°, showing no depression when mixed with the benzoylation product of tris(hydroxymethyl)phosphine oxide.

Preparation of the Barium Salt of Bis(hydroxymethyl)phosphinic Acid.—Three and eight-tenths grams of tetrakis(hydroxymethyl)phosphonium chloride dissolved in 100 cc. of water was boiled with 19 g. of barium hydroxide for several hours until the evolution of hydrogen ceased. The barium was then removed with a slight excess of sulfuric acid and the hydrochloric acid with silver carbonate. From the filtrate, dissolved silver was precipitated with hydrogen sulfide. The filtrate was then evaporated on the water-bath to a sirup and the heating continued for some time to drive off any formic acid which might have resulted from the action of barium hydroxide on formaldehyde. The acid was then converted into the barium salt by boiling with water and barium carbonate, the filtrate evaporated to small bulk and allowed to crystallize. The crystals were washed with a little water. The mother liquor seemed to contain caramel-like substances formed by the action of barium hydroxide on formaldehyde. The product consisted of well-developed crystals, moderately soluble in water, insoluble in alcohol.

Anal. Calcd. for $C_4H_{12}O_8P_2Ba$: Ba, 35.4; P, 16.02. Found: Ba, 35.2; P, 15.68.

Summary

The action of alkali on tetrakis(hydroxymethyl)phosphonium chloride has been shown to take place in two stages, giving first tris(hydroxymethyl)phosphonium oxide and finally bis(hydroxymethyl)phosphinic acid and liberating one molecule of hydrogen at each stage. With a neutral carbonate the action stops at the oxide stage.

Tetrakis(chloromethyl)phosphonium chloride was prepared from the corresponding hydroxy derivative by treating with phosphorus pentachloride. This was converted into tris(chloromethyl)phosphine and the latter to tris(chloromethyl)phosphine oxide.

A crystalline barium salt of bis(hydroxymethyl)phosphinic acid was obtained.

The work is being continued.

KEW GARDENS, NEW YORK

[CONTRIBUTION FROM THE LABORATORIES OF THE SHELL DEVELOPMENT COMPANY]

TRIORGANO THALLIUM COMPOUNDS. THALLIUM TRIETHYL AND THALLIUM DIETHYL TRIPHENYLMETHYL

BY H. P. A. GROLL

RECEIVED APRIL 21, 1930 PUBLISHED JULY 3, 1930

The only organo thallium compounds known are of the type R_2TlX,[1] *i. e.*, salts of the bases R_2TlOH first isolated by R. J. Meyer and A. Bertheim.[2] Many alkyl and aryl compounds of this type have been prepared by D. and A. E. Goddard,[3] E. Krause and A. v. Grosse.[4] F. Hein and E. Markert[5] and A. E. Goddard[3] attempted without success to prepare TlR_3 or $(Tl(C_2H_5)_2)_2$.

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[1] Hansen, Ber., 3, 3 (1870); Hartwig, *ibid.*, 7, 298 (1874).

[2] Meyer and Bertheim, *ibid.*, 37, 2051 (1904).

[3] Goddard and Goddard, J. Chem. *Soc.*, 119, 672, 1310 (1921); 121, 36, 256, 482 (1922).

[4] Krause and Grosse, *Ber.*, 58, 272, 1933 (1925).

[5] Hein and Markert, *ibid.*, 61, 2255 (1928).

A. v. Grosse[6] in his article "The Periodic System and the Alkyl Compounds of the Elements" predicts the existence of true thallium trialkyls from theoretical considerations of the atomic structure. In fact, no reason can be discerned why triorgano thallium compounds should not be stable provided the combination of the third valency of thallium with an organic radical can be achieved. The strongly alkaline character of dialkyl thallium hydroxide suggests that the third valency may be difficult to combine with an alkyl group, but as alkyls even of the alkali metals are known, it should not be impossible. The most promising method of combining the third valency with an alkyl group seemed to be reaction between thallium dialkyl chloride and an alkali metal alkyl, *e.* g.

$$(C_2H_5)_2TlCl + NaC_2H_5 = (C_2H_5)_3Tl + NaCl \qquad (1)$$

This reaction is analogous to Schlenk's synthesis of tetramethyl triphenylmethyl ammonium, and other penta-organo nitrogen compounds.[7] As both sodium ethyl and thallium diethyl chloride are insoluble in any indifferent solvent, this reaction presents many technical difficulties. Accordingly, lithium ethyl, which is soluble in petroleum ether, was chosen for the reaction. The reaction between lithium ethyl and thallium diethyl chloride occurs slowly with good yields and comparative freedom from side reactions at room temperature. Heating of the reaction mixture if only to 50° is unfavorable, as much metallic thallium is then formed.

Thallium triethyl is a heavy mobile liquid resembling lead tetraethyl in its odor and in many other characteristics. It differs in appearance from the lead compound in its bright golden yellow color, which becomes more intense at increased temperatures. At the temperature of carbon dioxide–acetone mixture the liquid is still yellow, but at liquid-air temperature it crystallizes to almost white crystals.

Thallium triethyl is soluble in ether, petroleum ether and alcohol, but is insoluble in water. Under atmospheric pressure it decomposes spontaneously at 129° before reaching its boiling point and liberates metallic thallium. Under a pressure of 1.5 mm. of mercury it boils unchanged at 54.8°, but it was observed that the compound decomposed if the temperature of the glass walls of the distilling flask rose to 90–100°.

The chemical properties differ more widely from those of the corresponding lead compound. Thallium triethyl is more reactive. While it is stable toward dry oxygen, it is decomposed readily by water to thallium diethyl hydroxide and ethane.

$$Tl(C_2H_5)_3 + H_2O = Tl(C_2H_5)_2OH + C_2H_6 \qquad (2)$$

This decomposition is comparatively slow, as the reaction occurs only at the interface between the two immiscible liquids. That the slow reaction is not due to inactivity of the thallium triethyl is shown by the fact that

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[6] Grosse, *Z. anorg. allgem. Chem.*, 152, 133 (1926).

[7] W. Schlenk and J. Holtz, *Ber.*, 49, 603 (1916); 50, 274, 276 (1917).

a much more rapid reaction occurs with alcohol, in which it is soluble. The compound is violently decomposed by absolute alcohol with evolution of heat and gas; also, when shaken with water it reacts much more rapidly, and in moist air emits white fumes due to reaction of its vapor with the water vapor.

For preliminary information prior to the preparation of thallium triethyl, thallium diethyl triphenylmethyl was prepared from thallium diethyl chloride and sodium triphenylmethyl, which latter is soluble in ethyl ether. The reaction occurred in the same way as with lithium ethyl. Thallium diethyl triphenylmethyl was obtained as a yellow sirup which did not crystallize. It therefore could not be separated from impurities such as triphenylmethyl carbinol and triphenylmethane. The sirup has properties similar to those of thallium triethyl. It is soluble in ether and petroleum ether, but insoluble in water. In moist air the sirup becomes coated with a skin of crystals which were shown to contain thallium. These crystals dissolve in water to give a solution with a strongly alkaline reaction, but are insoluble in ether or petroleum ether. They effervesce with acid and are obviously thallium diethyl carbonate. With water the sirup decomposes slowly without evolution of gas, the water becoming alkaline, and the sirup, originally clear and yellow, becoming cloudy and discolored. This indicates a decomposition to thallium diethyl hydroxide and triphenylmethane.

$$(C_2H_5)_2TlC(C_6H_5)_3 + H_2O = (C_2H_5)_2TlOH + HC(C_6H_5)_3 \qquad (3)$$

Thallium diethyl triphenylmethyl was not further examined since only a small quantity of it was prepared as a step toward the synthesis of thallium triethyl, the latter being the main object of this investigation.

Finally, it was found that thallium triethyl may also be prepared by direct reaction between ethyl chloride and alloys of thallium with sodium. Finely divided alloys containing 7, 10 and 15% of sodium were shaken for several hours with ethyl chloride. The reaction was very slow at room temperature. Small amounts of thallium triethyl were formed in each experiment but no way has been found to increase the yield.

Experimental

In the preparation of thallium triethyl from thallium diethyl chloride and lithium ethyl, oxygen and moisture must be rigorously excluded. The technique and apparatus used by Schlenk and Holtz[7,8] for the preparation of lithium ethyl were, with minor modifications, found suitable also for the preparation of the thallium triethyl. The thallium diethyl chloride must be as pure as possible. When the Grignard synthesis of the compound is carried out correctly, one recrystallization from ammonia is suf-

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[8] Schlenk and Holtz, *Ber.*, 50, **262** (1917). Houben–Weyl, "Die Methoden der organischen Chemie," Vol. IV, 2d ed., **p.** 959.

ficient; otherwise, a recrystallization in the dark from absolute alcohol, using conveniently a Soxhlet extractor, is necessary to provide a product pure enough for the synthesis. The lithium ethyl prepared by the reaction of finely granulated lithium with mercury diethyl was isolated by crystallization, weighed, and used as solid in order to ensure freedom from mercury diethyl, which would contaminate the thallium triethyl and be difficult to separate. This precaution is unnecessary if the solution of lithium ethyl as obtained by the synthesis is free from mercury. Lithium metal is prepared in a finely granulated form by melting lithium in white paraffin and stirring rapidly. Using such finely divided lithium, the yield of lithium ethyl with respect to mercury diethyl is practically quantitative.

Preparation of Thallium **Triethyl.**—Thirty-two and one-half grams (0.11 mole) of dry thallium diethyl chloride was put into a 200-cc. bulb of the type described by Schlenk with a neck wide enough to fill in the solid lithium ethyl by introducing the neck of the closed filter or storage bulb in which the lithium compound was weighed. Enough petroleum ether of 30–50° boiling range was added to cover the thallium diethyl chloride completely and to expel any air included by the powder. A stream of dry, highly purified nitrogen was passed through the bulb until all air was displaced. The bulb was inserted into a mixture of ice and salt to prevent reaction during the operation of filling. Six grams (0.16 mole) of lithium ethyl was added and washed down with petroleum ether, the bulb finally being filled to about two-thirds of its capacity. The neck and the side tubes were then sealed quickly, the stream of nitrogen being maintained as long as possible. For ease of operation in an inert atmosphere it is very convenient to use reaction bulbs with two side tubes set at 90° to each other instead of the bulbs with single tubes as described by Schlenk. The bulb was taken out of the ice and carefully shaken by hand for about twenty minutes. The temperature of the reaction mixture must not be allowed to rise above room temperature. Occasional cooling with ice was advisable during this period as the reaction sometimes started too rapidly. The bulb was then shaken in a shaking machine in the dark.

The liquid soon began to turn yellow and at the same time lithium chloride began to appear as a very fine light sludge, slightly discolored by traces of metallic thallium; the heavy powder of thallium diethyl chloride slowly disappeared. Completion of the reaction required twenty-four to forty-eight hours at room temperature, the time depending mainly on the fineness of the thallium diethyl chloride.

The bulb was opened in a stream of dry nitrogen and the liquid decanted into centrifuge tubes shaped at the top like a Schlenk bulb with a side tube for the nitrogen current. After centrifuging, the liquid was decanted from solid matter into another bulb. Any residual lithium ethyl was destroyed by passing through the solution a stream of dry air free from carbon dioxide. The liquid was filtered in a well-dried atmosphere and the petroleum ether removed by evaporation on a water-bath below 100". This evaporation may be accelerated by evacuating, a lower temperature being then maintained to prevent loss of thallium triethyl. The residue is pure thallium triethyl. The yield was 25 g. of $Tl(C_2H_5)_3$, *i. e.*, 79% of the theoretical. The product was distilled under vacuum and the constant-boiling fraction analyzed.

Analysis.—A weighed quantity (1.7144 g.) of substance was hydrolyzed with water and the amount of ethane formed according to Equation 2 measured. The solution was divided into five equal parts, one of which was titrated with 0.1 N hydrochloric acid to determine thallium diethyl hydroxide, while the other four were used for the gravimetric estimation of thallium as thallous iodide. The following gravimetric method was used.

The solution of $Tl(C_2H_5)_2OH$ was neutralized with dilute sulfuric acid and evaporated to dryness. The organic salt was decomposed by carefully adding fuming nitric acid and heating on a water-bath until no more red fumes were evolved. The solution was again evaporated to dryness, the residue dissolved in water, reduced with ammonium bisulfite and dilute sulfuric acid, and evaporated to dryness. The thallous sulfate was converted to thallous iodide as described by Fresenius.[9]

Anal. Subs., *1.7144:* C_2H_6, *0.1753.* Subs., *0.3429: 11.5* cc. of *N*/10 HCl. Subs., *0.3429:* TlI, *0.3897, 0.3857, 0.3907, 0.3889;* av., *0.3888.* Calcd.: C_2H_6, *0.1767; 11.76* cc. of *N*/10 HCl; TlI: *0.3898.*

Physical **Properties.**—Specific gravity, $S^{21.4}_{21.4}$, *1.971;* b. p. *54.6–54.8*° at *1.50–1.55* mm.; m. p. below −*80* and above −*183*°.

Thallium Diethyl **Triphenylmethyl.**—Two and four-tenths grams of dry thallium diethyl chloride was put into a bulb of the type already described. The air was then displaced from the bulb by dry nitrogen, *107* cc. of *0.075* N solution of sodium triphenylmethyl in ether was added and the mixture shaken until the red color of the sodium triphenylmethyl had disappeared. This took about twenty hours. The solution was separated from the precipitate by centrifuging in the manner already described and the ether evaporated.

The yield was about *4* g. of a yellow sirup, which contained much thallium. It was soluble in petroleum ether and in ether, and insoluble in water. It slowly decomposed in the presence of water without gas formation. After decomposition by water the extract with ether or petroleum ether contained no thallium, whereas the extract with water was strongly alkaline and gave all reactions of thallium diethyl hydroxide. From this behavior and analogy with thallium triethyl it is concluded that the sirup is or contains thallium diethyl triphenylmethyl. It was not further examined.

Summary

1. Thallium triethyl has been synthesized by the reaction of thallium diethyl chloride with lithium ethyl.

2. The chemical and physical properties of thallium triethyl are described.

3. Thallium diethyl triphenylmethyl has been synthesized from thallium diethyl chloride and sodium triphenylmethyl.

EMERYVILLE, CALIFORNIA

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[9] Fresenius, *Z.* anal. *Chem.*, **29–30,** *342 (1891).*

[CONTRIBUTION PROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

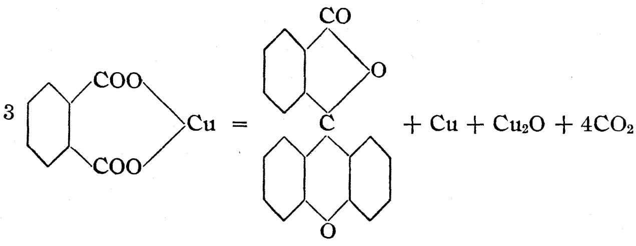
FLUORANE FROM THE DRY DISTILLATION OF COPPER PHTHALATE

BY JOHN B. EKELEY AND INEZ HAM MATTISON

RECEIVED APRIL 23, 1930 PUBLISHED JULY 3, 1930

In a previous paper,[1] mention was made of a product obtained by the dry distillation of copper phthalate, which was not further investigated at the time, being regarded as benzophenone from its appearance and odor. The yield seemed to be considerable and it was suggested that this might be a convenient method for the preparation of this ketone. A further examination, however, of the distillate obtained as described above reveals that the product is not benzophenone, but fluorane, and it may be obtained in yields as high as 91% of the theoretical.

It seems probable that the decomposition of the anhydrous copper phthalate takes place according to the equation



Experimental

Preparation of Copper Phthalate.—Copper carbonate was added to a hot water solution of phthalic anhydride until carbon dioxide was no longer given off. The solution was filtered and evaporated to crystallization. The copper phthalate crystals thus obtained were allowed to dry in the air. The moist crystals may not bc dried by heating them even at a relatively low temperature, since, if heated while wet, at a certain point in the crystalline mass they ignite and glow, the glowing quickly spreading through the whole decomposing mass. After the moist crystals had dried in the air, the anhydrous salt was obtained by heating them for some time at 120°.

Dry Distillation of Air-Dried and of Anhydrous Copper Phthalate.—Five grams of air-dried copper phthalate was distilled from a 50-cc. distilling flask upon the sand-bath, the flask being wrapped with asbestos and the receiver being cooled by means of a cloth wrapped around it and continually cooled with a stream of cold water. The flask was heated slowly at first and gradually raised to a dull red heat, and the heating continued until no more vapors passed over. Carbon dioxide was given off during the distillation. The residue left in the flask was a mixture of finely divided cuprous oxide and metallic copper, which when pressed out on a hard surface with a spatula showed the bright metallic luster of copper. The solidified distillate was crystalline and melted at 120°.[2]

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[1] Ekeley and Banta, THIS JOURNAL, 38, 767 (1917).

[2] R. Meyer, *Ber.*, 25, 1386 (1892). Fluorane crystallizes from alcohol solution with one-half molecule of alcohol of crystallization. In driving off the alcohol of crystallization in an air-bath at 120°, Meyer observed the curious fact that at 120°, after the

It was soluble in concentrated nitric and in concentrated sulfuric acid with a green-yellow fluorescence. An analysis gave the following results: Calcd. for $C_{20}H_{12}O_3$: C, 80.00; H, 4.00. Pound: C, 79.87; H, **4.22.**

Recrystallized from alcohol, it yields long bright prisms, which after giving off their alcohol of crystallization melt at 180°. The crystals gave the following analysis. Calcd. for $C_{20}H_{12}O_3 \cdot {}^1/_2C_2H_5OH$: C, 78.32; H, 4.64. Found: C, 78.08; H, 4.86. The substance is evidently fluorane.

Two grams of anhydrous copper phthalate was distilled very carefully. The fluorane obtained weighed **1.092** g., a yield of 91.5% of the theoretical.

The temperature of distillation must be above 300°. The quality of the distillate is only slightly influenced by the temperature, but much larger yields are obtained by strong heating.

Copper tetrachlorophthalate yields a similar distillate, but thus far the product has presented difficulties in the combustion for carbon and hydrogen and in the determination of chlorine. Presumably the product is dodecachlorofluorane, but checking analyses for carbon have not yet been obtained, since during the combustion small quantities of the compound distil through the red-hot copper oxide unburned and condense as minute crystals in the cold part of the tube. The combustion, while giving a low value for carbon, gives only a very small fraction of a per cent. of hydrogen, this latter corresponding to a dodecachlorofluorane, which would contain no hydrogen. The Carius method for chlorine yields varying low values for chlorine, around 58%, while the calculated value is **59.49%.** Other methods for chlorine also yield low results.

Summary

Dry distillation of anhydrous copper phthalate at high temperatures (between 300° and dull red heat) gives fluorane, which may be obtained in as high a yield as 91.5%.

BOULDER, COLORADO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF GRINNELL COLLEGE]

DECOMPOSITION OF OPTICALLY ACTIVE DIAZO COMPOUNDS[1]

BY FRANCIS EARL RAY

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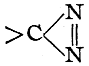
The aliphatic diazo group may be formulated as a straight chain or as a ring.

$>C=N\equiv N$



The chain structure was established largely by the work of Angeli,[2] Thiele,[3] and Staudinger,[4] who obtained chain derivatives of diazo compounds.

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alcohol had been driven off, a portion of the alcohol-free substance was ***melted,*** whereas the melting point of fluorane is 180°.

[1] Presented before the 79th meeting of the American Chemical Society, Atlanta, Georgia, April **10, 1930.**

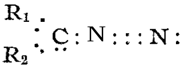
[2] A. Angeli, *Atti accad. Lincei,* [V] *32,* **i,** 443 **(1923).**

[3] J. Thiele, *Ber.*, 44, **2522 (1911).**

[4] Staudinger. *Helv. Chim. Acta,* **5, 75 (1922).**

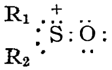
Recently there has been a disposition to revert to the ring structure. Lindemann and Thiele[5] as a result of studies of the parachors assign a ring structure to the azides, and Sidgwick[6] from a comparative study of boiling points is now inclined to favor the ring structure for both azides and diazo compounds. On the other hand, Mumford and Phillips[7] conclude that the parachor does not enable them to decide between the ring and chain formulas for the diazo group. Forster and Newman[8] had previously reached a similar conclusion.

If we assume a straight chain structure, then one of the carbon–nitrogen bonds is a polar valence and the other is a co-valence and together they form what is termed a semipolar double bond. The adjacent nitrogen loses one electron to the carbon and the asymmetry of the carbon atom results from a localization of this charge much the same as the localization of the ordinary bond is considered to cause asymmetry?



$\genfrac{}{}{0pt}{}{R_1\cdot}{R_2\cdot}\!:\underset{\cdot\cdot}{C}:N:::N:$

Quadrivalent sulfur compounds of the type



$\genfrac{}{}{0pt}{}{R_1\cdot}{R_2\cdot}\!:\overset{+}{\overset{\cdot\cdot}{S}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$

have been prepared and resolved into optical isomers,[10] showing that the positive charge is localized on the sulfur atom. The existence of a polar valence in quadrivalent sulfur was demonstrated by Sugden.[11]

In 1921 Levene and Mikeska[12] and in 1922 Noyes and Chiles[13] prepared optically active esters in which the only possible asymmetric carbon was that doubly bound to diazo nitrogen. This work has been criticized because the rotations of the compounds investigated were so small that impurities might have caused the observed rotation.

In 1926 Kendall and Noyes[14] obtained optically active diazo derivatives from both camphoric acid and *l*-isocamphoric acid. Camphoric acid and its derivatives, however, contain two asymmetric carbon atoms, but when strain is introduced into the molecule the secondary carbon only is racemized and the *l*-iso- compound is formed. Though Kendall prepared optically active diazo derivatives from both types of compounds, their instability precluded any decision as to the activity of the secondary carbon which was attached to the diazo group.

[5] Lindemann and Thiele, *Ber.*, 61, 1529 (1928).

[6] Sidgwick, J. *Chem. Soc.*, 1108 (1929).

[7] Mumford and Phillips, *ibid.*, 2112 (1929).

[8] Forster and Newman, *ibid.*, 97, 2572 (1910).

[9] W. *A.* Noyes, *Chem. Rev.*, 5, 549 (1928).

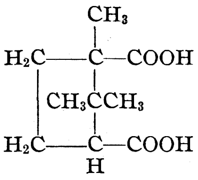
[10] Phillips, J. *Chem. Soc.*, 127, 1525 (1925); 2079 (1926); 188 (1927).

[11] Sugden, *ibid.*, 125, 1177 (1924); 127, 1528 (1925); 1173 (1927).

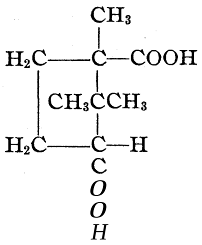
[12] Levene and Mikeska, J. *Biol. Chem.*, 45, 592 (1911); 52, 485 (1922).

[13] Chiles with Noyes, THIS JOURNAL, 44, 1798 (1922).

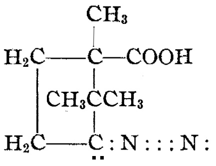
[14] Kendall with Noyes, *ibid.*, 48, 2404 (1926).



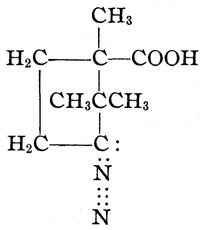
Camphoric acid (cis)



l-Isocamphoric acid (trans)



cis-diazo



trans-diazo

Skinner[15] has studied quite thoroughly the decomposition of aminolauronic ester, derived from the cis acid by substitution of the amino group for the secondary carboxyl; and Skinner and Noyes[16] have studied the decomposition of the trans-amino ester, similarly derived from the *l*-isocamphoric acid. They found for the decomposition of the cis-amino ester, 40 parts of hydroxy to 60 parts of unsaturated esters, and for the trans-amino ester, 60 parts of hydroxy to 40 parts of unsaturated esters. An ether acid was found only in the decomposition of the trans compound. There is, however, no direct proof that in these decompositions diazo compounds are formed as intermediates.

In this work we undertook to prepare the actual diazo compounds, to decompose them under identical conditions, and to study their decomposition products. By this method we have obtained definite evidence that the two compounds differ. From the decomposition of 20 g. of the *cis*-diazo compound we found 60.5% of unsaturated ester. This corresponds to the amount found by Skinner for the cis-amino compound. No ether acid was found.

In the decomposition products of the trans-diazo derivative we isolated the ether acid that Skinner found only in the decomposition of the *trans*-amino ester. Unsaturated esters were present to the extent of 27%.

A consideration of the conflicting physical evidence, together with the fact that the products of decomposition are partly the same, furnishes justification for the view that the chair and ring formulas represent tauto-

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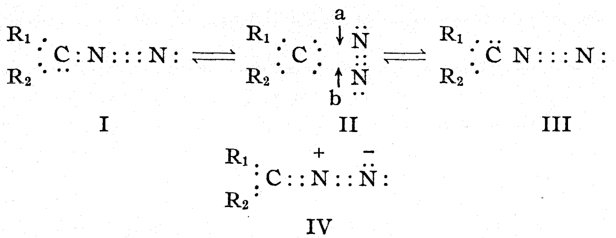
[15] **Skinner,** THIS JOURNAL, **45, 1498** (19[illegible]).

[16] **Skinner** *and* Noyes, *ibid.*, *39, 2692* ([illegible]).

meric modifications that exist in equilibrium. This would account for the ease with which the active form racemizes.



I II III

IV

The transition from the ring to the chain form may occur by a fission in the ring at either point (a) or at point (b). When the carbon–nitrogen bond breaks, the carbon must retain both electrons, for if both electrons went with the separating nitrogen, this nitrogen would be negative, the nitrogen adjacent to the carbon positive, and the compound optically inactive (form IV). If one of the electrons forming this severed carbon–nitrogen bond went with the carbon and the other with the nitrogen, neither the carbon nor the remote nitrogen would have a complete octet.

If the ring II opens at (a) then form III will result, while if fission occurs at (b), form I will be obtained. The carbon retaining the electrons being negative and the remote nitrogen positive, the free electrons on the nitrogen adjacent to the carbon will shift and occupy a place between the two nitrogen atoms. All atoms have completed octets in this interpretation.[17]

That we obtained different products on decomposition of the d- and *l*-forms was undoubtedly due to the slowness with which the active forms approach equilibrium at the low temperatures employed.

Experimental Part

***d*-Camphoric** acid was prepared by the oxidation of d-camphor with nitric acid. A total of fifty pounds of camphor was used in this work. The camphoric acid was converted into the anhydride by boiling with acetic anhydride. On heating with ammonium hydroxide under pressure by the method of Noyes and Taveau,[18] a mixture of the ammonium salts of a- and p-d-camphoramidic acids resulted which was separated by the difference in solubility of their ammonium and sodium salts.

Aminocamphonanic acid was obtained from the a-d-camphoramidic acid by means of the hypobromite reaction.

The anhydride of aminocamphonanic acid,  $C_8H_{14}\left\langle\begin{matrix}CO\\ | \\ NH\end{matrix}\right.$ was prepared by the method of Noyes and Potter[19] by heating aminocamphonanic acid with acetic anhydride and sodium acetate. It was also prepared by distilling the amino acid with chalk.

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[17] Lindemann, Wolter and Groger, *Ber.*, 63, 702 (1930), from a study of the parachors, refractive indices and absorption spectra also reach the conclusion that the diazo group is mostly cyclic but partly open chain that may exist in an optically active form.

[18] Noyes and Taveau, *Am. Chem. J.*, 32, 287 (1904).

[19] Noyes and Potter, This Journal, 37, 189 (1915).

The nitroso anhydride precipitated on passing nitrogen trioxide into the ice-cold aqueous solution of the amino anhydride. It was recrystallized from alcohol, giving light yellow needles, m. p. 138–139°; 60 g. of the pure compound was obtained. The rotation of 2.5 g. in 100 cc. of absolute alcohol was $[\alpha]^{24}_{D}$ 157.6°. Noyes and Potter give $[\alpha]^{24}_{D}$ 153°.

The cis-diazo derivative was prepared from the nitroso anhydride by the method of Kendall and Noyes,[20] which consists of treating the ethereal solution of the nitroso anhydride at 20° with sodium methylate. Light red crystals were obtained which melted, when pure, at 30–32° when placed in a bath at 25° and heated rapidly.

Twenty-one and two-tenths grams of the crystalline compound was obtained. On decomposition in ether solution with dilute sulfuric acid, 16.24 g. of material resulted. The ether solution was washed with dilute sodium carbonate solution to extract any ether acid but none was found.

From the 16.24 g. of material there was obtained by two refractionations 9.83 g. of unsaturated ester which boiled at 56° (3 mm.). The remainder boiled between 70 and 100°. A residue of 2.0 g. was left in the flask. The unsaturated ester, therefore, makes up 60.53% of the decomposition products (compare Skinner).

The trans-Derivatives

l-Isocamphoric acid was prepared by the method of Noyes and Knight,[21] in which d-camphoric acid is heated in sealed tubes with acetic and hydrochloric acids. A total of 1570 g. was obtained. This was converted into a,@-dimethyl*l*-isocamphorate which had the following constants: $[\alpha]^{25}_{D}$ −67.7"; d^{25}_{4} 1.0746; b. p. 117–118° (4 mm.). Noyes and Skinner give $[\alpha]^{24}_{D}$ 5 −65.5'. This dimethyl ester was hydrolyzed to the β-methyl *l*-isocamphorate, which was converted to the β-methyl a-trans-camphoramidate using the method of Noyes and Skinner.

Methyl *trans*-Amino-camphonanate.—Considerable difficulty was experienced in preparing this ester in good yield; 60 g. of the β-methyl a-trans-camphoramidate cooled to −20° was treated with 60 *g.* of bromine dissolved in a well-cooled 10% solution of sodium hydroxide. After standing for one hour, during which it had warmed up to 0°, it was heated for twenty to thirty minutes on the steam-bath. The oily layer which separated was extracted, dried, and distilled; yield, 30 g.; b. p. 112° (5–6 mm.).

Mono-urea from Methyl *trans*-Aminocamphonanate.—This compound was prepared by mixing 30 g. of methyl-trans-aminocamphonanate with a solution of 20 g. of nitrourea in 100 cc. of water.[22] On standing the mono-urea crystallized out and was recrystallized from alcohol; m. p. 155°.

Di-urea from Methyl *trans*-Aminocamphonanate.—The mono-urea was treated in ether solution with nitrogen trioxide forming the isocyanate. On adding an equivalent of methyl trans-aminocamphonanate crystals of the di-urea often separated. Sometimes an oil precipitated which was dissolved by adding more ether. Then on slowly adding 10% sodium hydroxide the di-urea precipitated in about 75% yield; m. p. 305°. This is the melting point obtained by Kendall and Noyes.

***Anal.* (Kjeldahl).** Subs., 0.1521 required 7.78 cc. of $N/10$ HCl. Calcd. for $C_{21}H_{36}O_5N_2$; N, 7.06. Found: 7.16.

Nitroso Derivative of Di-urea.—The di-urea was suspended in absolute ether at −20° and dry nitrogen trioxide was passed in for four to five hours. After standing overnight the ether solution was washed with ice water. Air was blown through the

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[20] Kendall with Noyes, THIS JOURNAL, 48, 2404 (1926).

[21] Noyes and Knight, *ibid.*, 32, 1670 (1910).

[22] Compare Davis and Blanchard, *ibid.*, 51, 1790 (1929).

mixture for about an hour, during which time the water was frequently changed. As the ether evaporated, crystals of the nitroso derivatives were deposited on the sides of the flask. On recrystallization from ether sulfur-colored, microscopic, rectangular plates melting at 78° were obtained. This compound is very unstable and tends to revert to the di-urea even when kept in a desiccator over calcium chloride. A Kjeldahl analysis gave results corresponding to the di-urea.

trans-Diazo Derivative.—The nitroso compound was dissolved in absolute ether and treated with one equivalent of sodium in absolute methyl alcohol. A deep red solution resulted. This was washed several times with water to remove the sodium hydroxide and the residual half of the urea molecule. The ether solution was then dried by freezing to −80" with a mixture of solid carbon dioxide and acetone. The clear ether solution was siphoned off and on evaporation the solid diazo resulted. It was not possible to purify this material by recrystallization, as the compound showed a tendency to decompose when warmed to about −15° and such attempts only resulted in making the material less pure. The purity of the diazo compound varied in the several runs from 89 to 92%. The diazo compound was decomposed by acidifying at −20° with dilute sulfuric acid. The ethereal solution was washed with sodium carbonate to extract the ether acid. The ethereal layer was dried, the ether distilled and the residue twice fractionated under reduced pressure; 32.12 g. of decomposition products gave 8.66 g. of unsaturated ester boiling at 90–95° (32 mm.). The remainder boiled at a temperature above 110". The unsaturated fraction9 make up 26.96% of the total.

Methyl Ether of cis-Camphonolic Acid.—The sodium carbonate extract was warmed with bone black, filtered, acidified and extracted with ether. The crystals from ether were recrystallized twice from alcohol and melted at 86–87°.

Anal. Subs., 0.0675: Ag, 0.0245. Calcd. for $AgC_{10}H_{17}O_3$: Ag, 36.86. Found: Ag, 36.30.

Since this paper was submitted for publication, additional evidence has been obtained showing that the cis and trans diazo compounds differ. Kendall[14] showed that the cis diazo compound spontaneously decomposed to give the bis-hydrazone of Noyes and Taveau,[13] m. p. 97°. When, however, the trans diazo compound was allowed to decompose in the same manner, a compound of high molecular weight (320–340) was obtained which melted at 71°. A mixed melting point gave 59–62°. These compounds may also be cis–trans isomers.

The writer expresses his thanks to the directors of the W. S. Hendrixson Memorial Fund of Grinnell College for a grant that defrayed part of the expenses of this investigation. Thanks are also due Miss Martha Hemphill and Mr. Ralph Bunting for the preparation of materials, to Dr. G. S. Skinner for gifts of camphoric acid and camphoric anhydride, and to Professor W. A. Noyes for his kindly interest and advice.

Summary

From a study of the decomposition of diazo derivatives of the methyl esters of both cis-aminocamphonanate and trans-aminocamphonanate, evidence has been secured that a carbon atom attached to the diazo grouping retains its asymmetry.

The methyl ether of cis-camphonolic acid is found only in the decom-

position products of the trans-diazo compound. The proportion of the unsaturated ester is different in the two decompositions.

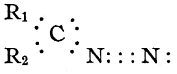
The two diazo compounds give by their decomposition approximately the following products: *cis*-diazocamphonanic methyl ester

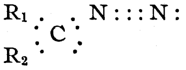
Esters of hydroxy acids	39.5%
Esters of unsaturated acids	60.5%

trans-diazocarnphonanic methyl ester

Methyl ether of cis-camphonolic acid	5.0%
Esters of hydroxy acids	68.0%
Esters of unsaturated acids	27.0%

The above results furnish conclusive proof that the two diazo compounds have an asymmetric structure, in part. This is most simply explained by the electronic formulas





GRINNELL, IOWA

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

NORMAL VALEROLACTONE. III. ITS PREPARATION BY THE CATALYTIC REDUCTION OF LEVULINIC ACID WITH HYDROGEN IN THE PRESENCE OF PLATINUM OXIDE

BY H. A. SCHUETTE AND RALPH W. THOMAS

RECEIVED APRIL 25, 1930 PUBLISHED JULY 3, 1930

n-Valerolactone has been prepared in the past by reducing levulinic acid to y-hydroxyvaleric acid and then removing the elements of a molecule of water from the latter. Reduction of the levulinic acid has been effected either through the agency of sodium amalgam[1] or of ethyl alcohol and sodium,[2] procedures which are time-consuming, expensive and ill-suited to the preparation of this lactone in quantity.

The basis for a simplification and an improvement in method of preparation was announced some years ago by Sabatier and Mailhe,[3] who by passing levulinic acid in gas phase together with hydrogen over a nickel catalyst at 250° succeeded in hydrogenating the former and dehydrating the resulting reaction product all in one operation. Certain facts[4] recently ascertained with respect to the stability of n-valerolactone at its boiling point having cast some doubt upon the quality of a product obtained at

[1] Wolff, *Ann.*, 208, 104 (1881).

[2] Losanitsch, Monatsh., 35, 301 (1914); Schuette and Sah, THIS JOURNAL, 48, 3163 (1926).

[3] Sabatier and Mailhe, *Ann. chim. phys.*, [8] 16, 78 (1909).

[4] Schuette and Thomas, THIS JOURNAL, 52, 2028 (1930).

this temperature, it seemed desirable, for this and other reasons, to investigate again the application of this form of hydrogenation to levulinic acid in the hope of harmonizing in principle Sabatier's procedure[3] with these newer observations. That this reduction can be carried out very conveniently at room temperature (22–24°) in the presence of platinum oxide[5] as catalyst, and that the rate of hydrogenation and efficiency of reduction are in this instance influenced by the solvent employed have been demonstrated in this Laboratory. The presentation of these facts is the object of this communication.

Experimental

For the purpose of making a comparison of the relative speeds with which the catalytic hydrogenation of levulinic acid[6] proceeds when the latter is dissolved in one of three common solvents (diethyl ether, ethyl alcohol, acetic acid), a series of reductions was made during the course of which several variables were introduced. What are deemed to be the most significant results of the series were obtained under the following conditions.

To 0.5 mole of levulinic acid in 150 cc. of anhydrous solvent there was added 0.4 g. of platinum oxide catalyst.[5] The usual form of mechanical shaker, operating at room temperature, was used with hydrogen under a pressure of 2.3 to 3.0 atmospheres. At the end of forty-four hours the reaction was interrupted because it was apparent that the consumption of hydrogen had practically ceased. Data pertinent to this series are presented in the form of curves (Fig. 1).

The best yield of lactone (87%), based upon the quantity of levulinic acid reduced, was obtained when ethyl ether was employed as solvent. Corresponding yields when ethyl alcohol and acetic acid were in turn substituted for the former proved to be *52* and 48%, respectively.

Anal. Subs., 0.2037: CO_2, 0.4449; H_2O, 0.1488. Calcd. for $C_5H_8O_2$: C, 59.97; H, 8.05. Found: C, 59.58; H, 8.17.

Physical constants were found to be n_D^{25} 1.4303; d^{25} 1.0465; M_{calcd}, 24.88; M_{found} 24.70:

During the course of a second series of reductions in ethyl ether solution fresh portions of catalyst were added at the end of seven and twenty hours, respectively. This modification of the procedure resulted in the theoretical yield of lactone at the end of forty-four hours.

Discussion

The reduction of levulinic acid proceeds in its initial stages approximately **3.5** times as fast in diethyl ether solution as when it is dissolved in ethyl alcohol, and 4.5 times as fast as in acetic acid. This statement is

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[5] Voorhees and Adams, THIS JOURNAL, 44,1397 (1922).

[6] Grateful acknowledgment is made to Milford A. Cowley for assistance given us in the preparation of the levulinic acid. This acid was made from sucrose, in part by the method of Rischbieth [*Ber.*,20, 1775 (1887)], and in part by the modified procedure of Conrad [*ibid.*, 11,2177 (1878); "Organic Syntheses," Vol. IX, p. 50].

based on the observation (Fig. 1) that at the end of seven hours, 0.27 mole of hydrogen was consumed when the reaction was being carried out in ethyl ether. The speed of reduction in ethyl alcohol was such that this quantity of hydrogen was not consumed until the reaction had proceeded for twenty-five hours and, similarly, in acetic acid for thirty-three hours.

That a reaction takes place between the acid and the solvent when reduction is carried out in the presence of ethyl alcohol was evident by the formation of some, as yet unidentified, ester. Glacial acetic acid is apparently inert in this respect since only the lactone and unreduced levulinic acid were found in the flask when the reaction had come to equilibrium.

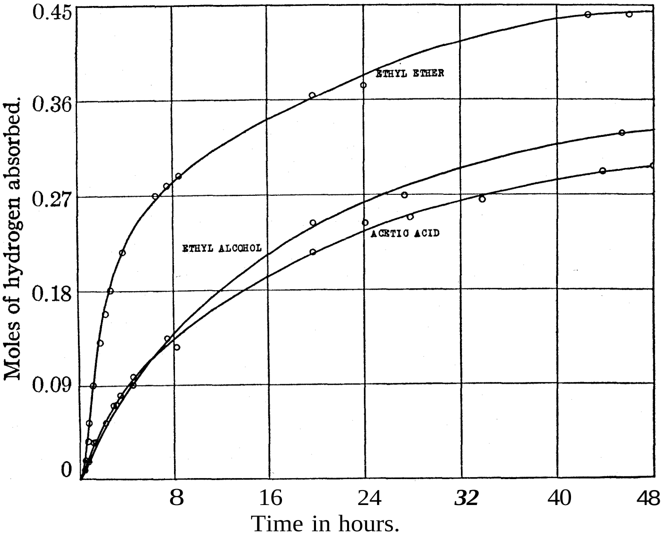

Fig. 1.—Effect of solvent upon the rate of hydrogenation of levulinic acid.

The superiority of diethyl ether over ethyl alcohol or acetic acid in this reduction lies not only in the production of larger yields of valerolactone, but also in the ease and certainty with which, because of marked differences in vapor pressure, solvent and reaction product can be separated.

Summary

The catalytic hydrogenation of levulinic acid can be most advantageously carried out at room temperature in the presence of diethyl ether as solvent. Theoretical yields of n-valerolactone are obtainable by this procedure.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

STUDIES IN THE CHLOROPHYLL SERIES. III. PRODUCTS OF THE PHASE TEST

BY J. B. CONANT AND W. W. MOYER

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One of the most characteristic reactions of the pure chlorophyll compounds is their behavior on treatment in ether solution with strong methyl alcoholic potassium hydroxide. In the "*a*" series the unallomerized chlorophyllides and the phaeophorbides give a yellow-brown color which soon changes to an intensive green. This appearance of a transitory characteristic color is known as the phase test. On diluting with water the material is found in the aqueous layer. In the "*b*" series the phase is reddish-brown instead of yellowish-brown. Although this method of saponifying the phaeophorbides is used as a test of the purity of the material, since the "altered" compounds do not give the characteristic yellow or red phase, the products of the reaction have been relatively little studied. Thus in Willstatter's directions for the saponification of the phaeophorbides[1] (phaeophytin) he recommends either treating the solid compound with hot or cold alcoholic potassium hydroxide or allowing a pyridine solution to react with alcoholic potash at the boiling point for half a minute. These procedures yield chlorin *e* (phytochlorin e), which has been the chlorin most studied. Another chlorin, phytochlorin g, is described in one paper by Willstatter[2] as being the principal product of the action of alcoholic potash on an ethereal solution of phaeophytin (phase test conditions). The chlorin was described as unstable and its transformation products were not isolated. It seemed to us a matter of interest to pursue this investigation further and we have done so, using the pure members of the "*a*" series.

Our first experiments were with methyl phaeophorbide a, prepared and purified according to the procedure outlined by Willstatter. The compound was dissolved in a small quantity of pyridine (20 cc. for each gram) and then diluted with much ether, so that the resulting solution contained 100 mg. in 150 cc. This solution was shaken vigorously with one-tenth its volume of a 25% solution of potassium hydroxide in methyl alcohol. The yellow color first appeared and gradually changed in the course of three minutes to bright green. In these concentrated solutions and on a large scale the yellow phase is never so bright as when a test with a more dilute solution is carried out on a small scale. At the end of five to ten minutes the mixture was diluted with water, the alkaline aqueous solution separated and the material in it transferred to fresh ether by acidification. The

[1] Willstatter and Stoll, "Investigations on Chlorophyll," translated by Schertz and Merz, Science Printing Co., 1928, p. **263**.

[2] Willstatter and Utzinger, *Ann.*, **382,** 129 (1911).

product was then fractionated by the usual Willstatter–Mieg procedure.

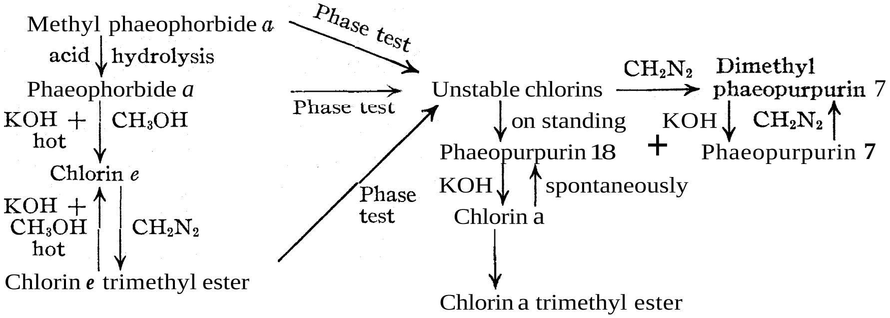
The major portion of the product was a mixture of chlorins in which unstable chlorins with acid numbers between 6 and 12 predominate. These chlorins cannot be isolated in a pure condition since they change more or less rapidly in ether solution, producing two compounds of a purplish brown color which we shall designate as phaeopurpurins. The two phaeopurpurins have acid numbers of 7 and 18, respectively, and crystallize readily; the yields from 1 g. of methyl phaeophorbide were, of phaeopurpurin 18, 350–435 mg., and of phaeopurpurin 7, 100–125 mg. In addition to the unstable chlorins which change into the phaeopurpurins, the phase test at room temperature yields approximately 150 mg. per gram of material of a stable chlorin fraction. This was composed of chlorin e (identified by conversion to the trimethyl ester with diazomethane) and a chlorin of acid number 5 containing one methoxyl group. The spectrum and behavior of the latter substance indicated that it might be a monomethyl ester of chlorin e but the action of diazomethane yielded an ester with different crystal form from the characteristic trimethyl ester of chlorin e.

At 23°, the phase test saponification is not complete in less than three minutes; five to ten minutes is a suitable time for preparative purposes. If the action is continued for five hours no phaeopurpurin 7 can be isolated; the products are chlorin e and phaeopurpurin 18.

The formation of chlorin e in the phase test can be completely suppressed by substituting ethyl alcohol or n-propyl alcohol for methyl alcohol in making the alcoholic solution of potassium hydroxide. The same result may also be brought about by carrying out the phase test at $-10°$. At this temperature the yellow phase persists much longer and the saponification is not complete even in fifteen minutes, but no chlorin e is formed. On the other hand, if the saponification of methyl phaeophorbide *a* is brought about by the action of boiling alcoholic potassium hydroxide in pyridine solution (Willstatter's procedure), chlorin e is the chief product and no unstable chlorins are formed. Thus by relatively slight changes in the conditions, the saponification of methyl phaeophorbide *a* yields either the unstable chlorins or the stable chlorins (chiefly chlorin e). With the same lot of methyl phaeophorbide we have been able to obtain the one type of product or the other; the phase test as ordinarily carried out at room temperature represents a set of conditions in between the two extremes but much nearer the optimum for the production of the unstable products.

We have found that the trimethyl ester of chlorin e is surprisingly like methyl phaeophorbide *a* in its behavior toward strong alkali. If one uses a dilute ether solution and methyl alcoholic potassium hydroxide, a yellow phase is distinctly visible; apparently this observation is new. The "phase" is somewhat slower in forming and persists longer than with the phaeophorbides. The product formed is a mixture of unstable chlorins which are identical in their behavior with those formed in the phase test with the phaeophorbides. Even at room temperature the unstable chlorins are the principal product and no chlorin e is formed, Just as in the case of the phaeophorbides, however, if the saponification is brought about rapidly at a higher temperature (using a pyridine solution and boiling alcoholic potash), no unstable chlorins are formed; the product was chlorin e, which was identified by the formation of the characteristic trimethyl ester on re-methylation.

The relationships of the phaeopurpurins to each other and the normal chlorophyll derivatives (phaeophorbides, chlorin e) is shown in the accompanying diagram.



Phaeopurpurin 7 contains a methoxyl group and at least one free carboxyl group. This is evidently the propionic acid group since it has been shown[3] that this is the free group in phaeophorbide *a*, and phaeophorbide *a* yields phaeopurpurin 7 through the phase test. The formation of dimethyl phaeopurpurin 7 by the action of diazomethane probably involves the esterification of one carboxyl and in addition an enol or carboxyl group. Phaeopurpurin 18 contains no methoxyl group, one free carboxyl group, and two masked carboxyl groups. The analyses indicate that there are but five oxygen atoms in the molecule, therefore a lactam and a lactone ring are probably present. One of these rings may be present in the closely related phaeopurpurin 7. The analyses indicate that in the conversion of the normal compounds (the phaeophorbides or the trimethyl ester of chlorin e) into phaeopurpurin 7, water has been added and that this water is eliminated in the formation of phaeopurpurin 18. The saponification of phaeopurpurin 18 yields a chlorin which appears to be identical with Willstätter's chlorin *a*. Its trimethyl ester is isomeric with the corresponding ester of chlorin e. Chlorin *a* slowly changes to phaeopurpurin 18 on standing; the process may be accelerated by heating a solution in a neutral solvent. Both the phaeopurpurins yield rhodoporphyrin on decomposition with alkali at 150°.

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[3] Conant and Hyde, THIS JOURNAL, 51, 3668 (1929).

The existence of more than one unstable chlorin in the products from the phase test is indicated by the wide range of acid number and by the spontaneous formation of both phaeopurpurin 7 and phaeopurpurin **18.** Probably two chlorins are present which differ only in a methoxyl group; the methoxy compound forms phaeopurpurin 7 spontaneously, the other yields phaeopurpurin **18** with loss of water. The action of diazomethane on the ether solution or dimethyl sulfate on the alkaline solution converts both of the unstable chlorins at once into dimethyl phaeopurpurin 7, as shown by the fact that the yield of this compound is equal to the combined yields of phaeopurpurin 7 and 18 when they are formed spontaneously. It seems probable that the unstable chlorin which yields phaeopurpurin **18** is identical with Willstatter's phytochlorin g. The method of formation is similar, the acid number approximately the same, and the instability is characteristic; we also found that our mixture gave an unstable red compound on heating with alcohol, as noted by Willstätter.[4]

We have summarized in Table I the empirical formulas which we consider most probable for the compounds described in this paper, and in the first paper of this series, together with representative analytical data. Each formula has been chosen to fit into a logical scheme and at the same time to give as good agreement as possible between the calculated and found percentages. When one makes due allowance for the difficulties of puri-

TABLE I

EMPIRICAL FORMULAS AND ANALYTICAL DATA

Name	Formula	Composition calculated				Analyses found			
		C	H	N	OCH_3	C	H	N	OCH_3
Methyl phaeophorbide a	$C_{36}H_{38}O_6N_4$	69.5	6.11	9.0	9.98	69.7	6.16	9.38	10.23
						70.38	6.23	9.32	10.58
Phaeophorbide a	$C_{35}H_{36}O_6N_4$	69.08	5.92	9.21	5.1	70.17	6.28	9.36	4.33
						69.11	6.16	9.43	
Methyl pyrophaeophorbidea	$C_{34}H_{36}O_3N_4$	74.45	6.57	10.22	5.66	74.20	6.98	10.1	5.54
						73.9	6.2		5.33
Pyrophaeophorbide a	$C_{33}H_{34}O_3N_4$	74.15	6.36	10.49	0	73.0	6.65	10.1	0
						72.6	6.33		
Phaeopurpurin 7	$C_{35}H_{38}O_7N_4$	67.1	6.07	8.95	4.95	67.26	5.92	8.74	5.19
						67.10	5.88	8.91	5.33
Dimethyl phaeopurpurin 7	$C_{37}H_{42}O_7N_4$	67.9	6.42	8.56	14.2	68.38	6.51	8.65	14.5
						68.46	6.28	8.53	
Phaeopurpurin 18	$C_{34}H_{32}O_5N_4$	70.85	5.55	9.72		70.18	5.87	9.26	0
	[$C_{34}H_{36}O_5N_4$	70.35	6.21	9.66]		70.04	5.64	9.85	
Methyl phaeopurpurin 18	$C_{35}H_{34}O_5N_4$	71.2	5.76	9.50	5.26	69.80	5.63	9.18	5.34
	[$C_{35}H_{40}O_5N_4$	70.5	6.71	9.40]		70.45	6.10	9.62	
Chlorin e	$C_{34}H_{36}O_7N_4$	66.70	5.88	9.15		66.7	6.4	8.8	
	[$C_{34}H_{40}O_7N_4$	66.3	6.5	9.10]		67.0	6.6	9.2	
Chlorin *e* trimethyl ester	$C_{37}H_{40}O_6N_4$	69.8	6.29	8.81	14.62	69.3	6.5	8.8	14.33
	[$C_{37}H_{44}O_6N_4$	69.4	6.88	8.75]		69.7	6.9	9.0	
Chlorin a	$C_{34}H_{34}O_6N_4$	68.7	5.72	9.43		68.2	6.4	9.04	
	[$C_{34}H_{38}O_6N_4$	68.25	6.36	9.37]		68.3	6.9	9.22	
Chlorin a trimethyl ester	$C_{37}H_{40}O_6N_4$	69.8	6.29	8.81		69.4	6.9	8.97	14.47
	[$C_{37}H_{44}O_6N_4$	69.4	6.88	8.75]		69.5	7.1	9.13	14.63

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[4] Ref. 1, p. 276.

fication and analysis of these compounds, the agreement is fairly satisfactory; the possibility of the compounds being richer in hydrogen must always be considered. This is particularly so in the case of phaeopurpurin 18 and its ester and chlorin a and its ester; the addition of four more hydrogen atoms to the empirical formulas would lead to a much more satisfactory agreement between the calculated and found compositions. This is shown in the table by the empirical formulas enclosed in brackets. Processes of reduction and oxidation may be involved in the transformations for which we have assumed merely saponification and hydrolysis. The formulas for pyrophaeophorbide a and methyl pyrophaeophorbide *a* have been derived from the parent compounds by assuming loss of carbon dioxide and formaldehyde since recent work in this Laboratory (which will be published shortly) has shown that the methoxyl group is involved in the thermal decomposition of the phaeophorbides.

Although it is too soon to attempt to write satisfactory structural formulas for the compounds involved in the phase test, certain facts are evident from our work. Both the phaeophorbides and the trimethyl ester of chlorin e must have in them a structure which is responsible for the formation of the unstable chlorins under the conditions of the phase test. This structure cannot be the lactam linkage which Willstatter postulated, since the results of the pyrolysis of chlorin e have shown the absence of a lactam ring in the compound. The opening of a lactone group might be involved but the mere opening and closing of such rings could not alone account for the shift of color to the phaeopurpurins. The functional groups themselves are apparently of no significance in determining the absorption spectrum, since pyrochlorin e from which two of these groups have been removed by pyrolysis has the same type of spectrum as the parent substance. Evidence in the same direction is afforded by the resemblance in color of the two phaeopurpurins, which nevertheless differ in the manner in which the potential carboxyl groups are combined. We are inclined to believe that while the changes involved in the normal series (phaeophorbides, chlorin *e*, and pyro-compounds) are due to changes in the functional groups, the transition to the other chlorins and phaeopurpurins is due to a reaction involving the unsaturated system in these molecules which, in contrast to that in the porphyrins, is very reactive.[5]

Experimental Part

Saponification under Phase Test Conditions of Methyl Phaeophorbide a.—One gram of methyl phaeophorbide ***a*** was dissolved in 20 cc. of pyridine, the solution diluted with 1500 cc. of ether, and 150 cc. of 25% potassium hydroxide in methyl alcohol added; the mixture was shaken vigorously for eight minutes. The yellow-green color of the phase appeared at the beginning and gradually changed to bright green. One liter of water was then added and the color at once changed to brown, all of the acidic material

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[5] Conant and Hyde, THIS JOURNAL, 52, 1233 (1930).

going into the aqueous layer, leaving the upper ether layer almost colorless. The alkaline water layer was acidified with dilute hydrochloric acid in the presence of fresh ether until all of the product was transferred to the ether. The ether solution, which was olive green in color, gave the following spectrum: 50 mm.: I, 706.9—646.1; II, 619.6—605.1 (hazy); III, 562; IV, 547.8- - -536.6—524; V, 513.6—483; E. A., 443. Order: I, V, IV, II, III.

The ether solution was then extracted with 6% hydrochloric acid until the blue color of the extracts began to diminish. The material in the acid extracts was at once retransferred to 800 cc. of ether. Spectrum of the 6% fraction in ether: I, 700- - -692.2—649.2; II, 617.1—604.1 (hazy); III, 536 2—528.4 (hazy at each side); IV, 511.4—486.7; E. A., 436.4. Order: I, IV, III, II. The residual ether solution then showed the following spectrum: I, 707.7—648.2; II, 618.9—606.2 (more prominent than in 6 per cent. spectrum); III, 544.8- - -533.8—524.1; IV, 512.2—484 8; E. A., 444.1; Order: I, IV, III, II. The solution was then further extracted with 9, 10, 11 and 12% acids successively. The extraction was stopped when the 12% extracts became only slightly colored. The acid solutions were of a deep green color. The ether solution from the combined extracts (1500 cc.) was olive green with a brownish tinge. Spectrum: I, 709.0—648.3; II, 620.6—605.7 (hazy); III, 546.8- - -534.5—524.3; IV, 512.6—484.4; E. A., 443.6; Order, I, IV, III, II. A small amount of material of a reddish-brown color was not extracted by even the 12% acid. The ether spectrum of it was: I, 717.6—652.3- - -628.2; II, 552.7—532.6; III, 514.0—497.4; IV, 482.5—471.2 (faint and hazy); E. A., 449.0; Order: I, II, III, IV. No attempt was made to isolate a pure substance from this product.

The two ether solutions from the 6% and 9–12% extractions were washed with water and allowed to stand over a small amount of anhydrous sodium sulfate for one week. At the end of this time the solution from the 6% extract was colored a greenish-brown and the other solution was a rich purplish-brown; each of these was then carefully fractionated according to the Willstätter–Mieg procedure.

The ether solution from the 6% extract was found to contain chlorin *e*, a monomethyl chlorin, phaeopurpurin 7, and a small quantity of phaeopurpurin 18. Chlorin *e* was removed with 3% acid, the monomethyl chlorin with 5% acid, phaeopurpurin 7 with 7% acid, while the phaeopurpurin 18 remained in the ether after extraction with 12% acid.

The other ether solution contained chiefly phaeopurpurin 18, together with some phaeopurpurin 7, which was removed with 7% acid. Extraction with stronger acids removed an intermediate fraction and a solution of pure phaeopurpurin 18 remained.

The yields from a number of experiments were 350–425 mg. of phaeopurpurin 18, and 100–125 mg. of phaeopurpurin 7. The total chlorin fraction was approximately 150 mg., and consisted of about an equal mixture of chlorin *e* and the monomethyl chlorin.

The same products were obtained by the saponification of phaeophorbide *a*. One run starting with 1 g. of phaeophorbide a and employing the procedure described above, except that phase-test alkali treatment was limited to three minutes, yielded the mixture of the two chlorins, 442 mg. of phaeopurpurin 18 and 72 mg. of phaeopurpurin 7.

The change in ether solution from the unstable chlorins first obtained to the brownish phaeopurpurin is very slow. The major part of the transformation takes place in two days, but at least a week is necessary to reach a state approaching completion. The ether solution may stand for two weeks or longer without decreasing the yields of phaeopurpurins. As described under the discussion of dimethyl phaeopurpurin 7, the same transformation may be brought about instantly by methylation with diazomethane.

The substitution of ethyl alcohol for methyl alcohol in the phase test results in a more rapid reaction and the formation of only the unstable chlorins, as the following experiment shows.

To a solution of 200 mg. of methyl phaeophorbide a in 300 cc. of ether (by use of pyridine) in a separatory funnel, was added 20 cc. of a 20% solution of potassium hydroxide in absolute ethyl alcohol. The yellow color of the phase appeared, but quickly turned green. The saponification proceeded with greater rapidity than when methyl alcoholic potash was used. A solid precipitated from solution. After shaking for four minutes, water was added. All the material went into the aqueous layer. The saponification products transferred to ether with a brownish-green color. Methylation with diazomethane produced the instantaneous color change to the phaeopurpurin color. After fractionation in the usual way, dimethyl phaeopurpurin 7 was obtained as the chief product; no chlorin e ester was found, the other product being weakly basic. In another experiment n-propyl alcohol was substituted for the methyl alcohol, the procedure being identical. Dimethyl phaeopurpurin 7 was obtained in excellent yields, no chlorin *e* ester being formed. The identity of the dimethyl phaeopurpurin 7 was checked by analysis.

A saponification at −10° was carried out as follows. A solution of 200 mg. of methyl phaeophorbide *a* in pyridine was transferred to 300 cc. of ether in a 500-cc. three-necked flask equipped with a mechanical stirrer and thermometer. The flask was surrounded by an ice–salt mixture and the ether solution cooled to −12°. Thirty cc. of a cold 25% methyl alcoholic potash solution was added and the mixture stirred mechanically for sixteen minutes. The temperature was kept at −10 to −12°. The mixture was then transferred to a separatory funnel and shaken with water. A small amount of unreacted methyl phaeophorbide *a* remained in the ether layer, but most of the material went into the aqueous solution. The alkali-soluble material was transferred to ether. The color of the ether was decidedly brown, and a treatment with 4% acid showed that no strongly basic chlorins were present. The ether solution was washed, dried and treated with diazomethane. The color became purplish-brown on methylation. The chief product was dimethyl phaeopurpurin 7. The side products were weakly basic materials of mixed green-brown color, not extracted by 10% acid. No chlorin e trimethyl ester was found. The yield of crystalline dimethyl phaeopurpurin 7 was 72 mg.

Phase Test Saponification of Chlorin e Trimethyl Ester.—A solution of 200 mg. of chlorin e trimethyl ester in 300 cc. of ether (the ester being first dissolved in pyridine) was shaken for fifteen minutes with 30 cc. of 25% methyl alcoholic potash. At the end of this time all the material was alkali soluble. Water was added and the product transferred to fresh ether. The color of the ethereal solution was a deep olive green with a brownish tinge; extraction with 4% acid showed the complete absence of any strongly basic chlorins. The ether solution was washed with water and dried with sodium sulfate. It was then shaken with an ethereal diazomethane solution until a test showed that all the material was alkali insoluble. Upon the addition of the diazomethane, the color of the solution changed at once to the rich purplish-brown color of the phaeopurpurins. On working up the product there was no trace of chlorin e ester; the chief product was dimethyl phaeopurpurin 7; the yield was 104 mg. It is interesting to note that chlorin *e* itself in an identical experiment yielded only the usual trimethyl ester and no phaeopurpurins.

Hot Saponification of Phaeophorbide *a*.—A solution of 600 mg. of phaeophorbide *a* in 2 cc. of pyridine was warmed to 80° in a silver crucible, and to this was added a boiling solution of 16 g. of pure potassium hydroxide in 25 cc. of methyl alcohol, while stirring with a silver spatula. The mixture was boiled for thirty seconds, cooled and washed with water in a separatory funnel. The reaction products in 1500 cc. of ether were completely methylated by diazomethane, and the esters were fractionally extracted with acid. The largest amount of material came out with 7 and 8% acid, and later proved to be chlorin e trimethyl ester. A very small amount of dimethyl phaeopurpurin 7 was found in the 10% extract. The remainder of the material was weakly basic chlorin esters which were extracted with 12–16% acid. The yield of chlorin e trimethyl ester (prismatic needles) was 320 mg.

Hot Saponification of Chlorin e Trimethyl Ester.—In a silver crucible, 138 mg. of the ester was dissolved in 0.4 cc. of pyridine. The crucible was warmed on a hot plate, and to it was added a boiling solution of 3.5 g. of potassium hydroxide in 6 cc. of methyl alcohol. The mixture was boiled for thirty seconds, cooled and washed into a separatory funnel with water. The saponification product was transferred to ether and the ether solution washed and dried. The olive-green chlorin solution was then completely methylated by means of diazomethane in the usual way. There was no change of color. No dimethyl phaeopurpurin 7 was found, but a small amount of weakly basic chlorin material remained in the ether mother liquor. The chlorin ester extracted by 8% acid, upon concentration of the ether solution, gave 74 mg. of chlorin *e* trimethyl ester as long prismatic needles, identical with the starting compound.

Properties of the Unstable Chlorins.—These compounds cannot be isolated in a solid state, as their solutions become brown on evaporation. The spectrum of the mixture as obtained by extraction with 9–12% acid and retransferring to ether was: I, 709.0—648.3; II, 620.6—605.7 (hazy); III, 546.8- - -534.5—524.3; IV, 512.6—484.4; E. A., 443.6; order I, IV, III, II. The action of diazomethane on this mixture and its spontaneous conversion to the phaeopurpurins is described below under these compounds. The ethereal solution on evaporating and boiling with alcohol gave a very unstable light red color similar to that described by Willstatter as characteristic of phytochlorin g. This red compound quickly changes to a mixture of the phaeopurpurins in which phaeopurpurin 18 predominates.

Monomethyl Chlorin from Phase Test Saponification.—The spectrum of this substance is identical with that of chlorin e trimethyl ester except for an extra line in the red. Spectrum (1 mg. in 30 cc.): I, 705—694; II, 683—646; III, 615—602; IV, 562- - -555; V, 545- - -534—526; VI, 512—485; E. A., 439. Order: II, VI, V, I, III, IV. The acid number is 5, and the acid solution is Flue. The ether solution is more green than that of chlorin *e*.

Anal. Calcd. for $C_{35}H_{42}O_6N_4$: C, 68.4; H, 6.84; N, 9.12; OCH_3, 5.05. Found: C, 68.14, 68.46, 68.64; H, 6.70, 6.61, 6.73; N, 9.26; OCH_3, 5.04, 5.07.

Phaeopurpurin 7.—This substance, purified by careful acid fractionation, is brown in ether solution, with a purplish tint. A thin layer of solution is more purple than brown. It crystallizes from ether in bluish-black spherical clusters of fine needles. It is very soluble in pyridine and acetone, almost insoluble in cold ether, insoluble in cold methyl and ethyl alcohols, but goes into solution upon heating, and is insoluble in petroleum ether. The acid number is 7, and the acid extract has a deep green color. The compound does not melt sharply, but fuses on the block at 200–205°. The spectrum was taken of an ether solution of a concentration of approximately 2 mg. in 50 cc. through a thickness of 50 mm. I, 714.0—648.6; II, 632.2—613.0 (faint and hazy); III, 549.6—526.8 (edges not sharp); IV, 514.1—487.4 (edges hazy); E. A., 443.4. Order: I, IV, III, II.

Anal. Calcd. for $C_{35}H_{38}O_7N_4$: C, 67.1; H, 6.07; N, 8.95; OCH_3, 4.95. Found: C, 67.10, 67.26, 67.57, 67.65; H, 5.88, 5.92, 6.54, 5.89; N, 8.74, 8.91; OCH_3, 5.19, 5.33, 5.45. (In these and all other analyses reported in this paper, the Pregl micro methods were employed; the samples were dried in high vacuum over phosphorus pentoxide for at least twelve hours at 61°.)

Dimethyl Phaeopurpurin 7.—An excess of diazomethane in ether was added to a solution of 80 mg. of phaeopurpurin 7 in 200 cc. ether. After two or three minutes the substance was completely methylated, as shown by shaking a portion of the solution in a test-tube with dilute alkali. The ether solution was fractionated and the product isolated in the usual manner; the yield was 55 mg. **A** more convenient method of preparation is to treat the mixture of unstable chlorins with diazomethane. Surprisingly enough, the color changes at once from olive green to the deep purplish-brown characteristic of the phaeopurpurins. The product is isolated in the usual way, care being taken in the acid fractionation to remove the trimethyl ester of a chlorin ***e*** with an acid number of 8. From 1 g. of methyl phaeophorbide *a*, 455495 mg. of crystalline dimethyl phaeopurpurin 7 may be thus obtained; 150 mg. of the trimethyl ester of a chlorin was obtained as a by-product. A third method of preparation is by alkylation with dimethyl sulfate. Two hundred mg. of methyl phaeophorbide ***a*** was saponified under phase-test conditions and the product transferred to 200 cc. of water in a separatory funnel. Then dimethyl sulfate, which had previously been washed with dilute alkali, was added a few drops at a time with continuous shaking. Each portion of dimethyl sulfate was used up before more was added. At the neutral point the methylated product began to precipitate from the solution and the solution became almost colorless. Small portions of dilute alkali were added to destroy any dimethyl sulfate that remained. The aqueous layer containing the precipitate was shaken with ether, the ester passing into the ether solution; it was separated from any unmethylated material by washing with 0.1 *N* alkali. The fractionation of this solution with 8 and 10% acids produced a small amount of chlorin ester and dimethyl phaeopurpurin 7.

Dimethyl phaeopurpurin 7 crystallizes from ether solution in glistening hexagonal plates of a purplish-blue color. The ether solution is purplish-brown and the acid solution is green. The acid number is 10. It is somewhat more soluble in solvents than phaeopurpurin 7, especially in ether. On a block it melts at 233–235°. Spectrum in ether (1 mg. in 25 cc.) 50 mm. tube: I, 712.1—650.8; II, 634.6- - -618.0 (very faint); III, 554.5- - -549.0—532.1- - -526.3; IV, 514.9- - -510.5—491.7- - -485.3; E. **A.,** 442.2. Order: I, IV, III, II.

Anal. Calcd. for $C_{37}H_{42}O_7N_4$: C, 67.9; H, 6.42; N, 8.56; OCH_3, 14.2. Found: C, 68.38, 68.46, 68.21; H, 6.51, 6.28, 6.44; N, 8.73, 8.65, 8.53; OCH_3, 14.45, 14.16.

Phaeopurpurin 18.—This substance, purified by recrystallization from ether, has a rich brown color in ether solution that shows a purplish tint in thin layers or dilute solutions. It crystallizes from ether in hair-like needles which form matted clusters and dark, irregular aggregates. The crystals are yellow-brown by transmitted light and dark blue by reflected light. The compound is difficultly soluble in ether and methyl and ethyl alcohol, insoluble in benzene and petroleum ether, easily soluble in pyridine, moderately soluble in acetone. The acid number is 18, and the acid solution is greenish-blue in color. It has no definite melting point but slowly sinters at 250–280° on the block. Spectrum: (1 mg. in 50 cc. of ether containing pyridine) I, 716.0—676.5- - -645.7—628.7; II, 549.9—544.2- - -540.5—533.8; III, 511.1—498.0 (shadow); IV, 484.4- - -470.7 (shadow, faint); E. **A.,** 436.8. Order: I,11,111, IV.

Anal. Calcd. for $C_{34}H_{36}O_5N_4$: C, 70.35; H, 6.21; N, 9.66. Found: C, 70.04, 70.18; H, 5.87, 5.64; N, 9.26, 9.85, 9.71; OCH_3, none.

Methyl phaeopurpurin 18 was prepared by the methylation of phaeopurpurin 18 with domiazethane in acetone solution. It crystallizes from ether in prismatic needles or long plates with pointed ends. The crystals are extremely insoluble in ether, but are fairly soluble in acetone and very soluble in pyridine. The color of the ester in solutions is similar to that of the free acid. The acid number is 19. It melts at 275–278° (block). Spectrum (1 mg. in 50 cc. ether): I, 717.1—675.1- - -645.9—628.5; II, 550—544.2- - -

540.0—533.7; III, 511.1—498.1; IV, 482.1—471.1 (shadow); E. A., 438.5. Order: I, II, III, IV.

Anal. Calcd. for $C_{35}H_{36}O_5N_4$: C, 71.0; H, 6.08; N, 9.46; OCH_3, 5.24. Found: C, 69.80, 70.15, 70.45; H, 5.63, 6.05, 6.10; N, 9.18; OCH_3, 5.34.

Chlorin *a*.—A solution of 300 mg. of phaeopurpurin 18 in 800 cc. of ether was shaken for ten minutes with 45 cc. of 25% methyl alcoholic potassium hydroxide; water was added and the product fractionated in the usual way. The 6–7% acid fraction was carefully refractionated to remove some material of lower acid number. Chlorin *a* crystallized from ether in clusters of small needles. The ether solution is slightly more greenish than that of chlorin *e*. The acid number is 6 and the acid solution is blue-green. The spectrum in ether (1 mg. in 30 cc.): I, 691.3—650.0; II, 620—606.2; III, 534—526.6; IV, 508.5—485.2; E. A., 432.5. Order: I, IV, III, II.

Anal. Calcd. for $C_{34}H_{38}O_6N_4$: C, 68.25; H, 6.36; N, 9.37. Found: C, 68.31, 68.20; H, 6.4, 6.9; N, 9.22, 9.04.

Chlorin *a* is the chief product, also, from the hot quick saponification of phaeopurpurin 18; there is also a small amount of a chlorin of acid number 3.5.

A sample of pure crystalline chlorin *a* after drying at 61° for twelve hours and standing for two weeks at room temperature was found to contain a small amount of phaeopurpurin 18. The transformation to phaeopurpurin 18 is hastened by heating as shown by an experiment in which a freshly purified sample was heated in diphenyl to 140° for thirty minutes; after transferring to ether the solution was purplish-red and a considerable amount of phaeopurpurin 18 was obtained by acid fractionation.

Trimethyl Ester of Chlorin *a*.—Methylation with diazomethane of the 6–7% fraction from the saponification of phaeopurpurin 18 (hot or cold) yielded the trimethyl ester of chlorin a. In one experiment 155 mg. was obtained from 300 mg. of phaeopurpurin 18.

This substance crystallizes from ether in hexagonal plates with a blue luster. The acid number is 10. The color of the ether and acid solutions is the same as those of the free acid. An ethereal solution does not show a "phase" with methyl alcoholic potash, but turns a deep blue-green color at once. The spectrum is the same as that of chlorin *a*. The melting point on the block was 239–240°.

Anal. Calcd. for $C_{37}H_{44}O_6N_4$: C, 69.4; H, 6.88; N, 8.75; OCH_3, 14.52. Found: C, 69.4, 69.54; H, 6.9, 7.13; N, 8.97, 9.13; OCH_3, 14.47, 14.63.

Alkali Decomposition of the Phaeopurpurins.—Thirty-milligram samples of both phaeopurpurin 7 and 18 were decomposed with 3 cc. of methyl alcoholic potassium hydroxide, 1.5 cc. of pyridine and 25 mg. of magnesium oxide at 150–160° for five hours in a silver-lined autoclave.[6] The resulting mixtures were shaken with 20% acid to decompose the magnesium complexes and transferred to ether. Fractionation showed that in each case rhodoporphyrin was almost the sole product. Only traces of material with acid numbers lower or higher than four were found. The 4% extracts gave solutions whose spectra in ether and acid solution were identical with those of a sample of rhodoporphyrin.

Summary

The saponification of methyl phaeophorbide *a*, phaeophorbide *a* and the trimethyl ester of chlorin e has been studied. Under phase test conditions at room temperature unstable chlorins are formed in large amounts; from these chlorins a new type of compound, designated as the phaeopur-

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[6] Treibs and Wiedemann, Ann., 471, 174 (1929).

purins, results by a spontaneous change. By the use of ethyl alcohol in place of methyl alcohol, or by lowering the temperature, the unstable chlorins became the sole products: quick saponification at an elevated temperature produces chlorin e and no unstable chlorins.

CAMBRIDGE, MASSACHUSETTS

NOTES

Attempted Use of Activated Silica Gel in the Esterification of Salicylic Acid and β-**Naphthol.**[1]—Korolev,[2] using an especially prepared silica gel suspended in the liquids, obtained 75–80% yields of methyl salicylate, and a 50% yield of methyl naphthyl ether.

Although the use of silica gel in the liquid phase seems to offer a simple method of preparing esters, the preparation of the silica gel as described by Korolev is far from a convenient process. It seemed worth while, therefore, to study the esterification of salicylic acid and 0-naphthol using silica gel which had been activated by passing dry air over the gel at a temperature of 150°, according to the commercial process as devised by Patrick (U. S. Patent 1,297,724) and which has been adapted to small-scale production by Holmes.[3]

Since silica gel activated in this way is known to be a good absorber of water, the presence of the gel should favor production of ester, not only by its catalytic powers, but also by removing the water formed.

The general method used was to place two samples of the mixture to be esterified in flasks fitted with reflux condensers and to heat them in a water-bath. Silica gel was added to one flask and, after refluxing for at least eight hours, the acid was then determined by titration with a standard base.

It was found that a number of different samples of silica gel activated by the method of Patrick do not catalyze the esterification of salicyclic acid or 0-naphthol with methyl alcohol.

CONTRIBUTION FROM THE
SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

R. CHELBERG
G. B. HEISIG

RECEIVED JANUARY 13, 1930
PUBLISHED JULY 3, 1930

Estimation of Organic Halogen.—In their paper "A General Method for the Determination of Halogens in Organic Compounds" [THIS JOURNAL, 52, 1195 (1930)] the authors, J. J. Thompson and U. O. Oakdale, make no mention in their references to a similar method

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[1] The experimental work was done by R. Chelberg, teacher of chemistry at Tracy, Minnesota.

[2] Korolev, *J. Chem. Ind.* (Moscow), 4, 547 (1927); C. *A.*, 22, 944 (1928).

[3] Holmes, "Laboratory Manual of Colloid Chemistry," 1922, p. 76.

[Robertson, *J. Chem. Soc.*, **107, 902** (1915); **109,** 218 (1916); *Chem. News*, **120,** 54 (1920)].

In their method fuming sulfuric acid alone or in conjunction with chromic acid or persulfate is used as oxidizing agent, and the liberated halogen absorbed in alkaline arsenite. In the present writer's method ordinary strong sulfuric acid and potassium dichromate are employed with aqueous sodium peroxide as absorbent. The following advantages are claimed. (a) The apparatus is much simpler; it is, in fact, an apparatus for the Bunsen determination of peroxides with slightly modified Peligot tubes for absorption. (b) The use of fuming sulfuric acid, an unpleasant reagent, is avoided. (c) As air is aspirated through the apparatus the time of an estimation is shorter, being fifty to sixty minutes instead of seventy to ninety as stated by Thompson and Oakdale. (d) Sodium peroxide is a reagent which has never been found to be contaminated with halogen.

In the last fifteen years some hundreds of estimations have been carried out by the author and his research students without a single failure. The method is described in various textbooks and is in use in a number of laboratories.

VICTORIA UNIVERSITY COLLEGE
WELLINGTON, NEW ZEALAND
P. W. ROBERTSON

RECEIVED MAY 13, 1930
PUBLISHED JULY 3, 1930

COMMUNICATIONS TO THE EDITOR

AN ATTEMPT TO DETERMINE NUCLEAR MOMENTS

Sir:

The explanation of the hyperfine structure of line spectra and the alternating intensities of band spectra involves the assumption of the existence of a proton spin in the nucleus of $^1/_2$ quantum unit. The magnetic moment associated with this spin would stand in the same ratio to the magnetic moment of the electron as e/m for the two charges. This means that the magnetic moment of a hydrogen nucleus would be 1/1840 of a Bohr magneton, which is too small an amount to detect in the ordinary Stern–Gerlach experiment.

In the case of the heavier atoms the proton spins are usually paired in the nucleus but in some cases, *e.* g., iodine, several protons remain unpaired and a resultant proton spin of several half units results. Thus a resultant spin of **3** units is to be expected for HI and 5 units for I_2. The iodine molecule has the larger spin, but the deflection in the Stern–Gerlach experiment is inversely proportional to the absolute temperature of the beam and the beam of iodine must be formed at room temperature while the beam of hydrogen iodide may be formed at a temperature of 130–140° K. Experiments were tried with both molecules.

In order to obtain the maximum deflection, pole pieces 10 cm. long were used to produce the inhomogeneous field. The beam was formed by slits of about 0.02 mm. width and was condensed upon a surface cooled with liquid air under reduced pressure. The image was photographed in *vacuo*. The image formed was about 0.2 mm. wide and under the most favorable conditions a broadening of the image of about 0.01 mm. was to be expected when the field was on. This effect should be easily measurable. The experiments failed because of the lack of sharpness of definition of the edges of the image. This lack of sharpness is partially the result of the long path of the beam. It was not possible to obtain images whose widths could be measured with certainty to 0.01 mm. and it is not certain that any deflection has been observed.

CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

W. H. RODEBUSH
W. A. NICHOLS, JR.

RECEIVED MAY 31, 1930
PUBLISHED JULY 3, 1930

CATALYSIS BY SODIUM CHLORIDE OF OXIDATION OF CARBON

Sir:

The catalytic action of salt in the oxidation of carbon, long familiar to the householder as a means of freeing chimneys of soot, may readily be demonstrated in the laboratory. If a glass tube or rod is held just above a flame which surrounds a wad of asbestos impregnated with sodium chloride, the latter volatilizes and deposits on the glass. A faint veiling is all that is necessary. An alternative method of applying the salt is to wipe a solution of it over the glass and let the water evaporate. Next, the glass is covered with soot by means of a smoky flame, over both the bare glass and that portion coated with sodium chloride, and is permitted to cool to give uniform temperature in the subsequent heating. If the tube or rod so prepared is then slowly heated, as uniformly as possible, it will be noted that the deposit of soot burns off first from the section where the sodium chloride is, leaving a very sharp dividing line between the treated and untreated glass surfaces.

A similar effect is observed if an effort is made to cover with soot a hot piece of glass, a portion of which has been treated with sodium chloride. Depending on the temperature, the soot will either fail to deposit at all on the treated surface, or will burn off rapidly when the smoky flame is removed, while the untreated glass becomes and remains covered.

An effort was made to follow the reaction quantitatively, using sugar charcoal heated to a definite temperature in a current of carbon dioxide-free air, determining the rate of formation of carbon dioxide by absorption in standard barium hydroxide solution. It was found that the uncatalyzed oxidation proceeded at an appreciable rate even at a temperature as low as 200°, and that the reaction was accelerated by the presence of sodium chloride; consistent rates, however, could not be obtained, since the reaction became slower and slower as time went on, presumably because of the more rapid oxidation at first of the smaller particles or more active patches on the carbon surface.

CHEMICAL LABORATORY
JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND
ROGER K. TAYLOR

RECEIVED MAY 31, 1930
PUBLISHED JULY 3, 1930

THE DECOMPOSITION OF HYDROCARBONS IN THE ELECTRODELESS DISCHARGE

Sir:

In the light of the recent note of Harkins and Gans [THIS JOURNAL, 52, 2578 (1930)] on the decomposition of benzene in the electrodeless discharge, the following observations may be of interest. In 1927 and 1928 the author, while at Yale University, collaborated with Dr. I. A. Black in a study of the spectra of some simple hydrocarbons. Several means of excitation were used in determining the most satisfactory method for producing a spectrum of the unaltered molecule; these methods are described in our paper on the spectrum of benzene [*Phys. Rev.*, 35, 452 (1930)]. Trial exposures using the electrodeless discharge were made on a number of substances including benzene, pentane, 2,2,4-trimethylpentane, acetylene, chlorobenzene and cyclohexane before the method was discarded because of the excessive decomposition it caused.

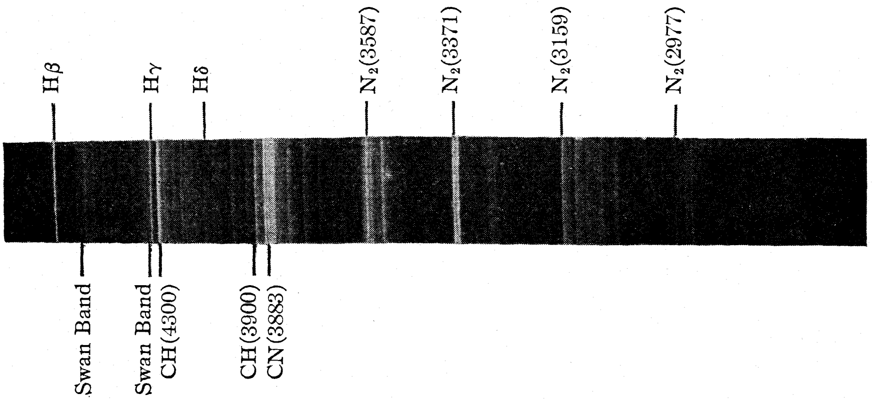

Fig. 1.—Spectrum of the decomposition products obtained from pentane in the electrodeless discharge.

Our photographs of benzene show complete agreement with the observations of Harkins and Gans. Three lines of the Balmer series of hydrogen, the Swan bands, as well as the CH bands at λ 4300 and λ 3900, and the line spectrum of ionized C were observed, the C line at λ 2478 being particularly prominent. All these bands and lines were produced by the other substances; in addition there appeared on most of the plates the second positive group of nitrogen, arising no doubt from the trace of air remaining in the discharge tube. The spectrum of pentane, shown in Pig. 1, and that of acetylene contained some bands which are believed to belong to the CN band group at λ 3883. In the case of chlorobenzene, a well-defined benzene spectrum appeared accompanied by faint "raies ultimes" of Cl at λ 4810, etc. These facts indicate that the process of breakdown in the electrodeless discharge is the same for all these simple hydrocarbons. It should perhaps be mentioned here that in every case save one relatively large amounts of reddish-brown product similar to that described by Harkins and Gans were obtained; the significant exception was cyclohexane by which only a little was produced. A more detailed discussion of these observations will appear in a future publication.

RESEARCH LABORATORY
UNITED STATES STEEL CORPORATION
KEARNY, NEW JERSEY
J. B. AUSTIN

RECEIVED JUNE 14, 1930
PUBLISHED JULY 3, 1930

NEW BOOKS

Anorganisch-chemisches Praktikum. Qualitative Analyse und anorganische Praparate. (Laboratory Manual of Inorganic Chemistry. Qualitative Analysis and Inorganic Preparations.) BY DR. E. H. RIESENFELD, Professor at the University of Berlin. Ninth edition, revised with the assistance of Dr. R. KLEMENT. Verlag von S. Hirzel, Leipzig, Germany, 1930. xvi + 393 pp. 29 figs. 13.5 × 20.5 cm. Price, M. 9.

The author points out in the Preface to this ninth edition of the "Praktikum" that it had been usual in German Universities since the time of Liebig and up to the first of this century to begin the study of experimental chemistry with analytical reactions and separations—that is, with qualitative analysis. In 1903, Haber brought back from his travels in this country the American method of instruction, according to which the student first carries out a number of simple experiments which portray before his own eyes the broad relationships of chemical phenomena. This method the author strove zealously to introduce during his teaching activities at Freiburg twenty years ago when the first edition of the laboratory manual was published. The author states that only during the last decade have a number of the large German Universities altered their procedure to the extent that they preface the instruction in analysis with some exercises in the preparation of chemical substances.

This manual as it has now been developed has after the customary discussion of laboratory manipulations a long chapter devoted to preliminary experiments illustrative of the broad principles of chemistry. Next are two chapters on the descriptive chemistry of the most important nonmetallic elements and one on the most important acids. Then follows a series of chapters based on the classification of systematic qualitative analysis. In each of these chapters there are experiments which develop both the general properties of the elements of the group and also those properties on which the analytical separation and detection are based. Meanwhile some sixty-four "preparations" are introduced at appropriate places. Discussions of the theoretical matters beyond what is given in the introductory chapter are also inserted at frequent intervals throughout the book.

It can be seen from the above that the manual combines the experimental work in general and inorganic chemistry with that in qualitative analysis and elementary inorganic preparations The experiments and preparations appear to be wisely chosen. The descriptions and explanations are clear and concise. The manual is now more complete than even a combination of the usual American manuals of general chemistry and qualitative analysis. A student who works through it conscientiously will acquire a thorough knowledge of inorganic chemistry and qualitative analysis.

ARTHUR B. LAMB

Annual Survey of American Chemistry. Vol. IV. July 1, 1928, to December 31, 1929. Edited by CLARENCE J. WEST, Director, Research Information Service, National Research Council. Published for the National Research Council by the Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1930. 549 pp. 13.5 X 21.5 cm. Price, $4.00.

Vol. IV of the Annual Survey of American Chemistry has been extended to cover a period of eighteen months in order that succeeding volumes of the survey may review the work published in a calendar year.

A study of the present volume brings out clearly the fundamental character and wide diversity of the contributions to chemical knowledge made in American laboratories. A recent compilation of statistics in regard to papers published on chemical subjects in the various countries of the world has shown that America and Germany head the list in the number of contributions. This volume is evidence of the high quality of the work done here.

The material presented is grouped in 43 chapters which have been prepared by active investigators in the several fields. In addition to the chapters dealing with the divisions of physical, inorganic, organic and industrial chemistry, this volume of the Survey contains reviews of work in certain limited fields in which rapid progress is being made. Among these are the following: determination of crystal structure by x-rays;

x-ray examination of industrial materials; carbohydrates; stereochemistry; pharmaceuticals; the vitamins; fermentation; rayon; synthetic resins. The extent of the work which is reviewed is evidenced by the fact that the index contains about 3500 names of authors. The activity in the several fields is shown by the number of references; for example, the chapter on insecticides and fungicides contains 249 references, fermentation 154, biochemistry 147, petroleum chemistry and technology 102, colloid chemistry 148, kinetics of homogeneous gas reactions 71.

It is evident that in this volume of the Survey the authors have succeeded in making their reviews more readable than in the past. When it was found advisable to refer to foreign work that had a direct bearing on the subject considered, such work has been included. Faced by the flood of contributions to chemistry that confronts one, the only way to keep in touch in a general way with current work outside one's own field is to read a book of the type of this Survey rather than to attempt to absorb knowledge from the usual form of highly condensed abstracts.

The Annual Survey of American Chemistry has made a place for itself and is steadily improving in its aim to present in a concise but readable form a record of the chemical research accomplished in this country.

JAMES F. NORRIS

Stuff. The Story of Materials in the Service of Man. By PAULINE G. BEERY. D. Appleton and Company, 35 West 32d Street, New York, 1930. xiii + 504 pp. Illustrated. 14.5 × 22.5 cm.

In this volume the author has written in a lively and enthusiastic vein about a great variety of materials or "stuffs," as she is at some pains to call them. She has been quite uncommonly successful in collecting a wealth of information of historical and "human" interest appertaining to these materials.

The presentation is descriptive and discursive. There is no progression and no attempt is made at any real explanation of chemical phenomena. There appear to be numerous inaccuracies: thus, we notice that "atomic numbers" are incorrectly defined; Prout is described as "a German chemist"; and Dalton's contributions are dismissed without mention of multiple proportions.

ARTHUR B. LAMB

Traité de Polarimétrie. (Treatise on Polarimetry.) By GEORGES BRUHAT, Professor in the Faculty of Sciences of Paris. Preface by A. COTTON. Éditions de la "Revue d'Optique théorique et instrumentale," 165 Rue de Sèvres; 3 and 5, Boulevard Pasteur, Paris, France, 1930. xvi + 447 pp. 250 figs. 16 X 24.5 cm. Price, 65 fr.

The subject of polarimetry is covered so thoroughly and so well in this treatise that the book will be invaluable to both the chemist and the physicist. It supplies to the chemist an excellent description of the various forms of polarimetric instruments and accessory apparatus, a very able presentation of the physical laws which underlie the subject and chapters on the related topics of magnetic rotatory power, rotatory dispersion and the rotatory power of crystals. The work is carefully indexed for subjects and authors and carries nearly nine hundred literature references.

C. S. HUDSON

Grundzüge der theoretischen und **angewandten** Elektrochemie. (Outlines of Theoretical and Applied Electrochemistry.) By Dr. GEORG GRUBS, Professor and Director of the Physical Chemical and Electrochemical Laboratories of the Technical High School of Stuttgart. Second, enlarged edition. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1930. xii + 495 pp. 165 figs. 16 × 23.5 cm.

At the time of the appearance of the first edition of this textbook [THIS JOURNAL, 46, 260 (1924)], which dealt with the electrochemistry of solutions, the avowed intention of the author was to issue a second companion volume covering the electrochemistry of molten salts and of gases. This program for various reasons was not carried out, but instead in this second edition chapters covering these subjects as well as the electrothermal processes used in the chemical and metallurgical industries have been incorporated. In addition, the chapters from the first edition devoted to the electrochemistry of solutions have been revised and enlarged. In particular, a discussion of theory of the complete dissociation of strong electrolytes has been introduced. This book is designed primarily to serve as a textbook for instruction in electrochemistry at colleges and universities. Thanks to its clear and reasonably concise presentation it appears admirably suited for that purpose.

ARTHUR B. LAMB

A Report of the National Research Council Committee on the Construction and Equipment of Chemical Laboratories. The Chemical Foundation, Incorporated, 654 Madison Ave., New York, N. Y., 1930. xiii + 340 pp. 124 figs. 15.5 X 23.5 cm. Price, $1.00.

The committee, consisting of G. L. Coyle, L. M. Dennis, C. R. Hoover, L. W. Mattern and J. N. Swan, has done a most valuable service in gathering under the covers of this excellent book the thought and experience of those who have produced some of the outstanding laboratory buildings erected before 1928. All phases of construction and of fixed equipment are considered. Advice is given on preliminary planning, location and exterior construction; this is followed by discussion of floor plans in general, ventilation, heating, lighting, plumbing, electrical installations and furniture. Various types of rooms such as must be provided in all larger chemical laboratories are described in detail, and there are special sections dealing with the problems of the high school, the chemical industries, biochemistry and various special fields such as microscopy and spectroscopy. With the authors, ten specialists have collaborated, and it is obvious that every effort has been made to secure information from all available sources. Particularly interesting is the section on Industrial Chemical Laboratories, in which the plan of an actual building is described and then discussed in detail. The book cannot fail to be invaluable to anyone who faces the task of planning a new building or, for that matter, to those responsible for the upkeep of older ones, not only because of its general survey of the topics mentioned above, but especially because of the discussion and description of smaller details which so often are overlooked by architects unfamiliar with the needs of chemical laboratories.

There are one or two suggestions that might be made for the improvement of the book in the new editions which seem likely to be demanded. In a few instances the material is not treated as specifically as is desirable. For example, the statement is made that several laboratories have made exhaustive tests of paints and enamels, but the laboratories are not named, and there are other instances of similar kind. One of the most difficult problems in planning a building is to decide on the ratio of connected load to total supply and to fix on reasonable load and diversity factors for the various supplies. In the case of electrical current this matter assumes major significance, for selection of too large values for the factors may involve the waste of thousands of dollars while the opposite error may prove the undoing of the whole system. Experience of engineers and architects who have never built a chemical laboratory is of no value. While it is true that these factors will differ for various types of laboratories, some information as to what has been done would be of great value. Likewise description of jumper boards or other types of local switchboards for increasing flexibility in the distribution of current would give the designer of a new building a starting point for his own plans. Flexibility in other respects, also, is of the utmost importance in the modern laboratory, especially if it is to provide for advanced work. The use of portable laboratory benches, of adjustable shelving, of openings in walls and floors for intercommunication between rooms has been successful in several buildings, and might have received more detailed discussion.

But these are relatively minor matters. The book will stimulate the building of better laboratories. By improving the facilities for instruction and research it will be a vital factor in the progress of chemistry.

H. I. SCHLESINGER

Lehrbuch der organischen Chemie. (Textbook of Organic Chemistry.) By Dr. PAUL KARRER, Professor at the University of Zurich. Second edition. Georg Thieme Verlag, Leipzig, Germany, 1930. xxi + 889 pp. 8 figs. 17 × 25 cm.

An examination of Karrer's "Textbook on Organic Chemistry" is interesting for a variety of reasons: It comes from the pen of an active and eminent organic chemist; it represents—"but little expanded"—a course of lectures given at a great university; the arrangement of the material is "based entirely upon didactic considerations"; and it met with such immediate favor that a second edition was required within two years.

The reviewer confesses that the first effect of a brief examination was a feeling of wonder, or better perhaps, of bewilderment. Here are more than 850 large and well-filled pages in which—to judge from a rough calculation based on the size of the index—more than 4000 organic compounds find at least mention. How, one wonders, is it possible to present all of this material in a year and perhaps also—how is it possible for the student to survive it?

A closer examination revealed a partial explanation of the mystery. The author concentrates on substances, "their origin, the proof of their constitution, and whenever possible, also the proof of their configuration." A few general topics like enolization, esterification and coordination compounds receive a measure of attention, but relatively little space is devoted to matters of this kind and to the mechanism of reactions. By a liberal use of charts, therefore, and a printed text for reference it would doubtless be possible to cover this extensive ground in a year.

In the choice of material for presentation the author was influenced by the needs of students of medicine and the circumstance that during the last two decades the major developments in organic chemistry have been associated with the problems presented by natural products. The text therefore contains very excellent chapters on fermentation, the carbohydrates, purines, terpenes and alkaloids, as well as on the dyes and their intermediates. In addition to the regular text the book contains eighteen pages of useful tables and an excellent index.

It is easy to understand why Professor Karrer's textbook has been so favorably received. Its contents are extensive and selected with skill, its arrangement is orderly, its style is clear and interesting, and the presswork is admirable. The book can be heartily recommended to American students as a book of reference for those who are taking a second course in organic chemistry.

E. P. KOHLER

Colloids. A Textbook. By H. R. **Kruyt**, Professor of Physical Chemistry, University of Utrecht. Translated from the manuscript by H. S. van Klooster, Professor of Physical Chemistry, Rensselaer Polytechnic Institute. Second edition, revised and enlarged. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1930. xiii + 286 pp. 118 figs. 15 X 23.5 cm. Price, $3.50.

The new edition is not greatly changed from the first edition,[1] either in quantity of material or method of presentation. Most of the topics have been brought up to date (September, 1929) by including reference to work published in the last few years. The author has successfully adapted the material treated to the understanding of students to whom it is addressed. The treatment of protein sols is admittedly "considerably at variance with the customary trend" and it is not obvious that this variance is justified by the experimental work quoted. One is surprised to read (p. 192) that the hydration of alcohol is governed by the law of mass action, which determines the equilibrium between the alcohol hydrate(~)and their decomposition products; and it is almost a shock to read (p. 263) that "we can compute the activity coefficient, i, according to the formula of van't Hoff," from the boiling point elevation of a soap solution. Instances of such loose statements are rare and perhaps they should not be mentioned at all.

As in the previous edition, the translator has successfully rendered a foreign language into smooth English from which literal translations of foreign idioms are happily lacking.

E. B. MILLARD

Kapillarchemie. **Eine Darstellung** der Chemie der Kolloide und verwandter Gebiete. (Capillary Chemistry. A Treatise on the Chemistry of Colloids and Related Fields.) By Prof. Dr. **Herbert Freundlich**, Kaiser Wilhelm Institute of Physical **Chemistry** and Electrochemistry. Fourth edition, revised with the assistance of J. Bikerman. Akademische Verlagsgesellschaft m. b. H., Schlossgasse 9, Leipzig C 1, Germany, 1930. viii + 566 pp. 97 figs. 17.5 X 25 cm. Price, unbound, M. 36; bound, M. 39.

The present new (fourth) edition is to appear in two volumes instead of one. The first volume is devoted to the fundamental principles of colloid chemistry; the second will presumably contain the remainder of the subject matter of earlier editions, namely, a discussion of individual colloid-disperse systems.

The first volume as compared with the corresponding part of the second edition, which appeared in 1922, shows only an enlargement of about 4% but it is clear that there have been a thorough revision and a careful consideration of recent work. This is particularly evident in the section dealing with interfacial films, where there has been so much active research.

As for the sub-division into two volumes, it is undeniable that two

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[1] Reviewed in THIS JOURNAL, 49, 1852 (1927).

moderate-sized volumes in place of the single bulky volume of the earlier editions are a convenience. On the other hand, there is the resultant extra cost, a matter of real moment at the present time when the cost of scientific literature is mounting to such heights. Moreover, the indices present a difficulty: a separate index for the second volume would not only cause inconvenience but would detract from the value of the handbook as a whole; on the other hand, a combined index in the second volume would render the present index occupying 56 pages useless and hence an unnecessary expense.

However, irrespective of the cost, this revision of so unique, important and useful a handbook will be welcomed by the host of students and investigators interested in this rapidly developing field.

ARTHUR B. LAMB

Essential Chemical Elements that Constitute a Balanced Food. By CHARLES NOYES KINNEY, A.C., M.S., Professor of Chemistry in Drake University. Second edition. Success Composition and Printing Company, Des Moines, Iowa, 1930. xvi + 303 **pp.** 15.5 X **23.5 cm.**

The first edition of this book was issued in 1929, and the second edition came from the press in the first half of 1930, which is a rather short time to elapse between the first and second editions. The second edition has been enlarged and contains 315 pages. The author states that it is the purpose of this book to review the newer ideas on foods and to clarify somewhat the discussion that is taking place on the subject at this time. It is the hope of the author that the data contained in the book will aid the reader to obtain a clearer conception of what constitutes a food for animals. There are twelve chapters and the title of each chapter is put in the form of one or more questions pertaining to the nature and function of the various metallic and non-metallic elements that ordinarily occur in a normal food. The author emphasizes the possible function of minute quantities of such elements as manganese, copper, zinc, nickel, cobalt, barium, strontium, fluorine, bromine and iodine in organic combination in the economy of plants and animals. Small quantities of compounds of these elements are normal constituents of the earth's crust and plants absorb minute quantities from the soil and synthesize them into metal and non-metal organic complexes, some of which undoubtedly have the properties of enzymes, oxidases, peroxidases, catalases, hormones and vitamins. The contents of the various chapters consist for the most part of abstracts of recent articles occurring in research journals dealing with the metabolism of plants and animals. The book should find its most interested readers among research investigators in these subjects. The book contains an appendix, a glossary of the less familiar words and terms pertaining to medicine, pharmacy and chemistry.

J. S. MCHARGUE

The Journal of the
American Chemical Society

VOL. 52 AUGUST, 1930 No. 8

[Contribution from the Laboratory of General Chemistry of the University of Wisconsin]

PROMOTER ACTION IN REACTIONS OF OXIDATION CONCOMITANT WITH THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE.[1,2]

I. THE OXIDATION OF HYDRAZINE

By Donald P. Graham

Received November 19, 1929 Published August 5, 1930

Introduction

The catalytic decomposition of hydrogen peroxide by iron and copper salts has been studied in this Laboratory by Bohnson and Robertson,[3] who observed that when a slight amount of a copper salt was added to the iron salt used as the catalyst, a marked promoter effect was observed. This was explained by Robertson as being due to the fact that cupric acid reacts with hydrogen peroxide much faster than does ferric acid.

Walton and Christensen[4] showed that the oxidation of ethyl alcohol by hydrogen peroxide catalyzed by ferric salts was dependent on the same mechanism as that shown by Bohnson and Robertson to effect the catalytic decomposition of hydrogen peroxide. They were, however, unable to extend the parallel into the study of promoter action because the catalytic activity of the copper salts was inhibited by the presence of the ethyl alcohol. The purpose of this investigation is to extend these studies into fields that permit the investigation of the phenomenon of promoted oxidation concomitant with the catalytic decomposition of hydrogen peroxide by iron and copper salts. The oxidation of hydrazine is particularly well adapted to mechanistic studies of this nature as it does not interfere markedly with the action of the catalysts used.

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[1] This work is from a thesis presented by the author in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin, conducted under the personal direction of Professor James H. Walton.

[2] This research was made possible by a grant from the Research Committee of the University of Wisconsin, Dean C. S. Slichter, Chairman.

[3] Bohnson, *J. Phys. Chem.*, 25, 19–54 (1921); Bohnson and Robertson, This Journal, 45, 2493 (1923); Robertson, *ibid.*, 47, 1299 (1925).

[4] Walton and Christensen, *ibid.*, **48**, 2083 (1926).

Browne and Shetterly[5] and others have pointed out that when hydrazine is oxidized by concentrated solutions of hydrogen peroxide, appreciable side reactions occur which result in the formation of considerable ammonia and some hydrazoic acid. However, preliminary experiments by the author showed that in the presence of the catalysts used the oxidation of hydrazine gave a yield of 98–100% nitrogen, justifying the equations

$$2H_2O_2 = 2H_2O + O_2$$
$$N_2H_4 + O_2 = 2H_2O + N_2$$

Experimental Part

Materials.—The hydrogen peroxide was obtained as Merck's Superoxol **(30% H_2O_2)** and was twice distilled at diminished pressure to remove all preservatives. It was stored in quartz.

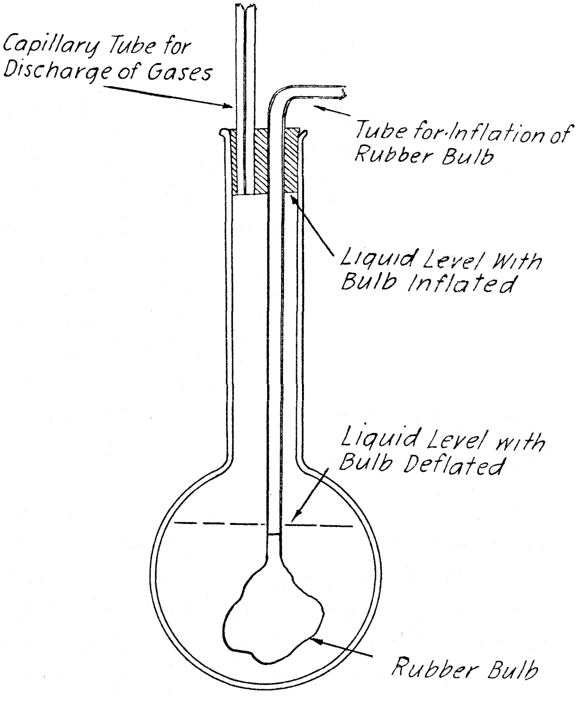

Fig. 1.—Reaction flask.

Pure copper sulfate, ferric sulfate and hydrazine sulfate were available and were used without further purification.

The water used for the dilution of samples was obtained from the laboratory distilled water supply and redistilled in glass over barium hydroxide.

Apparatus and Method.—The hydrogen peroxide with hydrazine sulfate and catalysts was placed in a flask which was shaken with a shaking machine[6] which permitted

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[5] Browne and Shetterly, THIS JOURNAL, 31, 783–99 (1909).

[6] Walton, *Z. physik Chem.*, 47, 185 (1904).

the gases $N_2 + O_2$ to be evolved as soon as they were formed. The speed of the reaction was determined by measuring the rate at which these gases were evolved. The nitrogen contained in the gas evolved is a measure of the extent of the oxidation of the hydrazine and the estimation of this nitrogen necessitated the complete removal of the gas mixture from the reaction flask. This was effected by means of the rubber bag as shown in Fig. 1. By inflating the immersed rubber bag, it was possible to raise the liquid level to the top of the reaction flask and drive all the gas in the system into a gas buret. This gas mixture was then run repeatedly into alkaline pyrogallol until all the oxygen was absorbed. The remaining nitrogen was then measured in a gas buret, affording a measure of the extent of the oxidation of the hydrazine at the time when the gas was driven from the reaction flask. This time was carefully noted, making it possible to study the extent of the oxidation as a function of time. Since the nitrogen evolved is equal in volume to the oxygen consumed in the oxidation, the total volume of the gas evolved in the reaction is a true measure of the extent of the decomposition of the hydrogen peroxide.

Results

In this study the decomposition of the hydrogen peroxide and the concomitant oxidation of the hydrazine were studied as functions of time. In each run a volume of 120 cc. of solution was used, containing one millimole of hydrazine sulfate, hydrogen peroxide sufficient to give on decomposition 125 cc. of oxygen referred to standard conditions and the catalyst in quantities as noted. All runs were carried out at a temperature of 25.0°. The results obtained were checked by duplication. The decomposition of hydrogen peroxide was followed with an accuracy of about 3%, while the measurement of the rate of evolution of nitrogen was accurate to about 5%. These accuracies were sufficient to establish the relationships sought.

It was found that neither the first- nor second-order type of reaction was completely fulfilled in these reactions but it was observed that toward the middle of the reaction, a first-order constant was closely approached. This is shown in Table I and was found true in the oxidation of the hydra-

Table I

The Oxidation of Hydrazine by Hydrogen Peroxide Catalyzed by 0.200 Millimole of Copper Sulfate. Data for the Decomposition of Hydrogen Peroxide Referred to Standard Temperature and Pressure

Time in minutes	Cc. of gas mixture evolved	(a)	$(a - x)$	10^4K
00	00	125.0	125.0	..
16	35.3	125.0	89.7	3.46
25	50.5	89.7	74.5	3.44
30	57.5	74.5	67.5	3.32
36	65.0	67.5	60.0	3.26
40	69.0	60.0	56.0	2.83
46	74.5	56.0	50.5	2.90
60	85.5	50.5	39.5	2.90
75	94.5	39.5	30.5	2.88
End	125.0			

K as mean of last four values. 2.88.

zine and also the decomposition of the hydrogen peroxide. Because of the space required the original data are not given in detail, but are summarized in tables and graphs thoughout the text. For both reactions it was found that when the extent of reaction was plotted against time the graphs obtained were of the same type for various catalyst concentrations, so it was quite feasible to employ the constants as obtained above as measures of the reaction velocity. These computations were made using the second as the unit of time.

Copper Sulfate as a Catalyst.—The reactions under consideration were studied with various concentrations of copper sulfate and the results obtained are summarized in Table II. They are also given graphically in Pig. 2.

TABLE II

COPPER SULFATE AS A CATALYST

Concn. of $CuSO_4$, millimoles	0.05	0.100	0.150	0.20	0.30	0.50	0.70	1.00
10^4K	.443	.865	1.59	2.88	5.60	14.2	25.6	43.6
$10^4K'$	.320	.71	...	1.96	4.05	...	...	...

K, Reaction rate for decomposition of hydrogen peroxide.
K', Reaction rate for oxidation of hydrazine.

These results indicate that the mechanism of the oxidation of hydrazine is closely related to that of the decomposition of hydrogen peroxide since variations in catalyst concentration effect the same trends in both reactions.

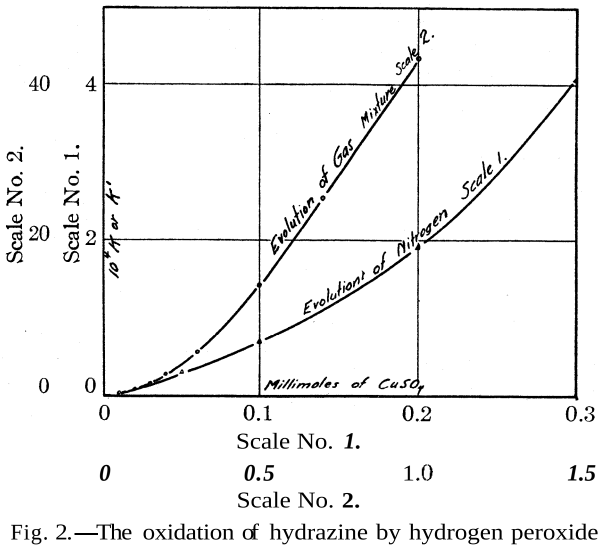

Fig. 2.—The oxidation of hydrazine by hydrogen peroxide catalyzed by cupric ions.

The accompanying graph shows that at concentrations of copper sulfate below **0.50** millimole an increase in catalyst concentration produces an increase in the rate of decomposition of the hydrogen peroxide, the slope of the curve increasing with increasing concentrations of copper sulfate. However, at higher concentrations the relationship is linear. This effect may be explained by the possibility that a compound may be formed between the hydrazine sulfate and the copper salt, there being exactly 1.00 millimole of the hydrazine salt present. It was not found practicable to carry the study of this effect into the oxidation of the hydrazine as the reaction velocity was so high at these catalyst concentrations that accurate readings were impossible.

Ferric Sulfate as a Catalyst.—Ferric sulfate was studied as a catalyst in a manner similar to that employed with copper sulfate. In this work, the milliatom, abbreviated as ma. and equal to one-half a millimole, was used as the unit of concentration. This was due to the fact that the active catalyst is assumed to be the ferric ion and not the ferric sulfate molecule. The results are summarized in Table III and Pig. 3.

TABLE III

FERRIC SULFATE AS A CATALYST

Concn. of $Fe_2(SO_4)_3$, milliatoms	**0.20**	**0.40**	**0.50**	**0.70**	**1.00**	**1.50**	**2.00**
10^4K	**.39**	**.61**	**.74**	**.90**	**1.19**	**1.62**	**2.4**
$10^4K'$	**.20**	..	**.35**	..	**0.52**	**0.78**	..

As in the case of copper sulfate, the reaction of oxidation follows closely that of the decomposition of the hydrogen peroxide, indicating that in this reaction, as in the one previously treated, the oxidation of the hydrazine is effected through the decomposition of the hydrogen peroxide and must be explained by the same mechanism established for this decomposition. The relationship is shown clearly in Fig. 3. There are also indications of compound formation as were observed with copper sulfate except that the first part of the curve showed a constantly decreasing slope indicating that the effect tends to accelerate the reaction. This effect was observed for the decomposition of the hydrogen peroxide and for the oxidation of the hydrazine as well, offering excellent confirmation of the suggested parallelism between these two reactions.

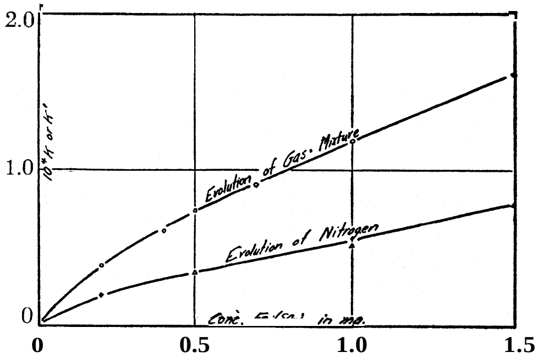

Fig. 3.—The oxidation of hydrazine by hydrogen peroxide catalyzed by ferric ions.

Cuprie Sulfate Used in Various Concentrations with 0.200 Ma. of Ferric Sulfate as Catalyst.—Far the purpose of detecting and studying the phenomenon of promoter action, the study of the catalytic properties of mixtures of ferric and cupric sulfates was undertaken next. In these studies, the concentration of one of the catalysts was fixed while that of the other was varied. For the first group of runs it was found convenient to fix the ferric sulfate concentration at 0.200 ma. and to vary the copper sulfate concentration. The results obtained are given in Table IV and are graphed in Fig. 4.

TABLE IV

CUPRIC SULFATE USED IN VARIOUS CONCENTRATIONS WITH 0.200 MILLIATOM OF FERRIC SULFATE AS CATALYST

Concentration of $CuSO_4$, millimoles	0.00	0.05	0.10	0.15	0.20
10^4K	.39	1.47	2.84	5.4	10.1
$10^4K'$	.20	0.78	1.6	2.8	4.3

It was found that the mixtures of catalysts studied showed a total effect much greater than additive. The quantitative expression of this promotion will be considered in a later portion of this paper. It is, however, immediately apparent that these results differ from those of Robertson, who found that the greatest effect relative to the copper concentration was obtained with the smaller quantities of the copper salt while these results show that in the presence of hydrazine sulfate the promoter effect continues with increased concentrations of the copper salt. These relationships are made more apparent in the quantitative discussion of the promoter action. The effect was observed both for the decomposition of the hydrogen peroxide and for the oxidation of the hydrazine.

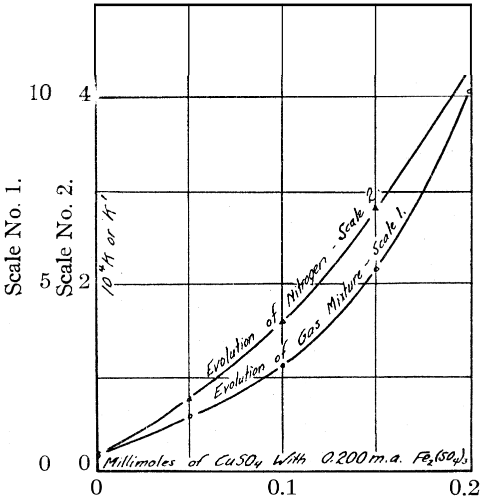

Fig. 4.—The oxidation of hydrazine by hydrogen peroxide catalyzed by 0.200 ma of ferric sulfate with various quantities of cupric sulfate.

Ferric Sulfate Used in Various Concentrations with 0.100 Millimole of Cupric Sulfate as Catalyst.—Continuing the study of the catalytic activity of mixtures of ferric and cupric sulfates, the reaction velocities were determined for a group of runs in which the concentration of cupric sulfate was fixed and that of the ferric sulfate varied. The results are summarized in Table V and in Fig. 5.

As before, in this group of runs, a marked promotion was observed. However, as can be seen by comparison of Fig. 5 with Fig. 4, the effect of

TABLE V

FERRIC SULFATE USED IN VARIOUS CONCENTRATIONS WITH 0.100 MILLIMOLE OF CUPRIC SULFATE AS CATALYST

Concn. of $Fe_2(SO_4)_3$ in milliatoms	0.00	0.200	0.400	0.700	1.00	1.50
10^4K	.87	2.8	5.0	6.3	7.7	9.2
$10^4K'$	.71	1.63	2.1	2.4	..	..

increasing the concentration of cupric sulfate was quite different from that observed when the concentration of ferric sulfate was the variable studied. In general it was observed in the study of mixtures of the two catalysts that when the concentration of one was varied, the reaction rate for both the decomposition of the hydrogen peroxide and for the oxidation of the hydrazine followed the general trends observed when that catalyst was used alone in varying concentrations.

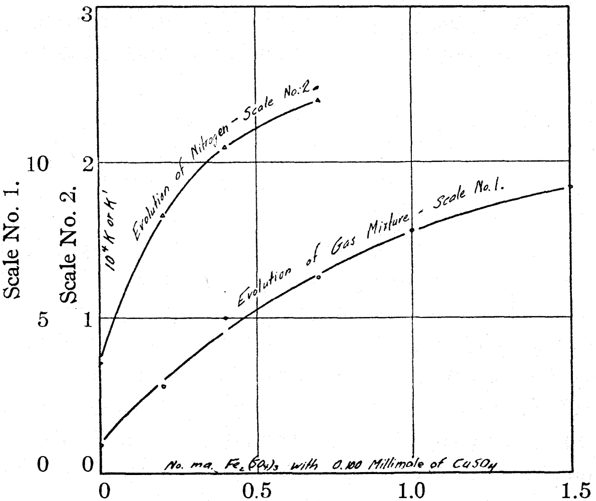

Fig. 5.—The oxidation of hydrazine by hydrogen peroxide catalyzed by *0.100* **millimole of copper sulfate with various quantities of ferric sulfate as noted.**

The Effect of Acidity.—The effect of the addition of various quantities of sulfuric acid to the reaction system was studied with copper sulfate and ferric sulfate used individually and in combination as catalysts for the oxidation of hydrazine by hydrogen peroxide. The results obtained showed the effect on the reaction to parallel closely that on the decomposition of the peroxide, offering still further evidence that these two reactions are dependent upon the formation of the same catalytic intermediates. An increase in acidity resulted in an inhibition of the two concomitant reactions quite similar to that observed in the earlier studies of the catalytic decomposition of hydrogen peroxide by iron and copper salts.

A Quantitative Measure of Promoter Action.—Attention has been called in an earlier part of this paper to the fact what when the two catalysts ferric sulfate and cupric sulfate are used together, the resulting rate is greater than the sum of the rates obtained when the same catalysts are used separately. In order to obtain a mathematical evaluation of promotion, the following conventions are employed

K_{t} = reaction rate for mixture of catalysts
K_{fe} = reaction rate for ferric sulfate at concentration noted
K_{cu} = reaction rate for copper sulfate at concentration noted

$$A = \frac{(K_{\text{t}} - K_{\text{fe}})\ (0.200)}{(K_{\text{cu}})\ (\text{Concn. ferric sulfate})} = \text{promotion factor for cupric sulfate}$$

$$B = \frac{(K_{\text{t}} - K_{\text{cu}})\ (0.100)}{(K_{\text{fe}})\ (\text{Concn. cupric sulfate})} = \text{promotion factor for ferric sulfate}$$

For the reaction of the decomposition of hydrogen peroxide, the symbols are used as above but for the oxidation of hydrazine, the letters are primed, as A' and B'.

The promotion factor for cupric sulfate as defined by the above formula is the ratio of the increase in the rate of reaction effected by its addition to a reaction system already containing 0.200 milliatom of ferric sulfate, to the reaction velocity effected by its use as a catalyst in the absence of the ferric sulfate. Likewise, the promotion factor for ferric sulfate is the ratio of the increase in reaction velocity resulting from its addition to a reaction system already containing 0.100 millimole of copper sulfate, to the reaction velocity obtained by its use alone as a catalyst. Since the promotion factor of each catalyst is referred to a certain definite concentration of the other, this factor will change with variation in catalyst concentration. The last term in the numerator together with the last term in the denominator form an approximating correction term for the concentration of the reference catalyst. Since this correction term is only approximate, assuming a linear relationship, the true values for A and A' are reached only from the data obtained with the ferric sulfate concentration fixed at 0.200 milliatom, when the correction term becomes unity and drops out of the computation. Likewise, the true values of B and B' are obtained only from the data obtained with the cupric sulfate concentration fixed at 0.100 millimole.

Promotion factors computed by the method just discussed from the data obtained in the studies of the catalytic effects of the mixed catalysts are given in Tables VI and VII.

It is evident that the approximating factor introduced gives satisfactory results in the computation of B and B' but gives values deviating markedly from the true values in the computation of A and A' in Table VII. Although the true values of the promotion factors show slight trends, it is entirely practicable within the concentration limits studied to express these relationships as constant. The averages of these values are $A = 3.0$; $A' = 1.8$; $B = 5.5$; $B' = 4.5$.

TABLE VI

PROMOTION FACTORS OBTAINED WITH 0.200 MILLIATOM OF FERRIC SULFATE WITH VARIOUS QUANTITIES OF CUPRIC SULFATE AS NOTED

	Concn. of $CuSO_4$ in millimoles			
	0.05	0.10	0.15	0.20
A	2.5	2.8	3.1	3.4
A'	1.8	2.0	1.6+	2.1
B	5.3	5.1	6.5	9.4
B'	4.6	4.6	4.0	5.7

TABLE VII

PROMOTION FACTORS OBTAINED WITH 0.100 MILLIMOLE OF CUPRIC SULFATE WITH VARIOUS QUANTITIES OF FERRIC SULBATE AS NOTED

	Concn. of $Fe_2(SO_4)_3$ in milliatoms				
	0.20	0.40	0.70	1.00	1.50
A	2.8	2.5	1.8	1.5	1.2
A'	2.0	1.3	0.8	...	...
B	4.9	6.7	5.9	5.6	5.2
B'	4.7	4.8	4.1	...	...

The Mechanism of the Oxidation.—It has been shown that hydrazine is oxidized by hydrogen peroxide in the presence of ferric sulfate or copper sulfate or mixtures of the two, and that all factors tending to affect the rate of decomposition of the hydrogen peroxide have a similar influence on the rate of oxidation of the hydrazine. This inter-relationship is so complete that there is no doubt that the oxidation is facilitated through the formation and decomposition of the same intermediates that have previously been shown to effect the decomposition of the hydrogen peroxide, namely, ferric and cupric acids. The qualitative facts cited above, however, do not give definite evidence as to whether the oxidation is due to reaction of the hydrazine directly with these catalytic intermediates or with the oxygen released in the reaction of the hydrogen peroxide with the ferric and cupric acids. The hydrogen peroxide is in too dilute a solution to effect alone a measurable portion of the observed oxidation in the period of time involved. It seems probable that the oxidation is effected by both of the suggested possible means. Of the two catalytic intermediates, the ferric acid must be considered the stronger oxidizing agent because it will react with a cupric ion to form cupric acid. This is not conclusive evidence, however, that the oxidation velocity would be the greater, although it is hoped by means of the promotion factors to show that this is the case. The phenomenon of promotion alone is strong evidence that the oxygen released in the reaction of the ferric or cupric acid with hydrogen peroxide plays a very marked role in the oxidation of the hydrazine, because a mixture of oxidizing agents such as ferric and cupric acids, except as they might react with each other, would not show more than additive effects. The, hydrogen peroxide is present in such a relatively high concentration as would make reaction of a molecule of ferric acid with a molecule of cupric acid quite infrequent. Even if they did react, the oxygen liberated would probably be less potent than that liberated by the reaction of either cupric or ferric acid with hydrogen peroxide because, as has been previously cited, hydrogen peroxide is capable of forming either cupric or ferric acid from a lower state of oxidation. The fact that the promotion factors for the decomposition of hydrogen peroxide are much larger is some indication that the oxidation is not entirely due to the oxygen evolved in the reaction of the hydrogen peroxide with the ferric or cupric acids but that these catalytic intermediates may act directly as oxidizing agents, an increase in the rate of their decomposition rate resulting in a decrease in their oxidizing efficiency. It was observed that the ratio of A to A' was much greater than the corresponding ratio of B to B'. ($A/A' = 1.65$ and $B/B' = 1.22$.) This is quite definite indication that the oxidizing power of ferric acid is greater than that of cupric acid. This relationship may perhaps be clarified by saying that the addition of ferric sulfate to a reaction system already containing a certain mixture of both catalysts produces a certain increase in the rate of decomposition of the hydrogen peroxide and also a definite increase in the rate of oxidation of the hydrazine, and that the addition to the same original reaction system of enough cupric sulfate to effect the same increase in the rate of the decomposition of the hydrogen peroxide will result in a smaller increase in the rate of oxidation of the hydrazine than did the ferric sulfate. This may seem at variance with the fact that when the catalysts are used separately, the ratio of $K'_{\text{cu}}/K_{\text{cu}} = 0.73$ from Table II, and from Table III the ratio $K'_{\text{fe}}/K_{\text{fe}} = 0.48$. (These are average values.) However, this fact does not necessarily condition the behavior of these two catalysts when used together because, as has been suggested by Robertson, the ferric acid acts on the cupric ion to form cupric acid more rapidly than does hydrogen peroxide alone.

Summary

1. The oxidation of hydrazine by hydrogen peroxide catalyzed by ferric sulfate, cupric sulfate and various mixtures of the two has been studied and found to be comparatively free from side reactions.

2. The effects of the variation of catalyst concentrations were studied for the individual catalysts and for various mixtures of the two. Attention was given both to the reaction of the decomposition of the hydrogen peroxide and the oxidation of the hydrazine. When the catalysts were used separately, copper sulfate was found to be a much more effective catalyst than ferric sulfate for both reactions.

3. The phenomenon of promoter action was found to enter into both

the decomposition of the hydrogen peroxide and the oxidation of the hydrazine, and promotion factors were computed.

4. The effect of acidity was studied and observed to be quite analogous to the inhibition noted in studies of the decomposition of hydrogen peroxide in the absence of hydrazine.

5. The mechanism of the oxidation of the hydrazine is probably as follows. The hydrazine is oxidized both by the oxygen liberated in the reaction of the catalyst intermediate with the hydrogen peroxide and by that catalyst intermediate itself. When ferric and cupric sulfates are used together, producing both cupric and ferric acids, the ferric acid is more effective in the oxidation than is the cupric acid, the observed promotion in the oxidation reaction being almost wholly due to oxidation by the evolved oxygen which is liberated in an activated state.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

REACTIONS IN LIQUID HYDROGEN SULFIDE. VIII. SPECIFIC CONDUCTANCE OF LIQUID HYDROGEN SULFIDE

BY S. D. SATWALEKAR, L. W. BUTLER[1] AND J. A. WILKINSON

RECEIVED JANUARY 20, 1930 PUBLISHED AUGUST 5, 1930

Introduction

There is but little agreement in the published values for the specific conductance of liquid hydrogen sulfide. Steele, McIntosh and Archibald[2] reported it as being an extremely poor conductor and gave the value for the specific conductance as about 0.1×10^{-6} at $-81°$. Magri[3] found it "much less than 4×10^{-7} at $-60°$." Quam and Wilkinson[4] concluded from qualitative observations that it was much less than this, being less than 1×10^{-11} reciprocal ohms. Borgeson,[5] using a sensitive Wheatstone bridge set-up, obtained values varying from 10^{-6} to 10^{-8} at $-78.5°$.

In view of these varying results it was the purpose of this work to make a quantitative determination of the specific conductance of liquid hydrogen sulfide at $-77°$.

Experimental

The liquid hydrogen sulfide was prepared in the apparatus described by Quam.[6] The conductivity cell was made from a wide test-tube with a stopper through which passed the glass tubes making mercury connections

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[1] Assistant Professor of Physics at Iowa State College.

[2] Steele, McIntosh and Archibald, *Phil. Trans.* Roy. *Soc.*, **205A,** 99 (1906).

[3] Magri, *Atti Accad. Lincei,* [5] *16, I,* 510 (1907).

[4] Quam and Wilkinson, THIS JOURNAL, 47, 989 (1925).

[5] Borgeson, unpublished data from this Laboratory.

[6] Quam, THIS JOURNAL, 47, 103 (1925).

with the platinum electrodes sealed into them. The electrodes were of sheet platinum (3.25 X 2 cm.) and these were held rigidly in place about a millimeter apart by fine glass rods set between them and sealed together at the ends. This arrangement permitted the easy removal of the electrodes from the cell for cleaning. They were cleaned with mixed acids, washed with water, platinized, washed with water, alcohol and ether and dried with warm air. A mark was made on the test-tube where the volume was 20 ***cc.,*** about 1 cc. above the tops of the electrodes, and the cell was filled to this mark each time.

The conductivity set-up included several dry cells as a source of electromotive force, a D'Arsonval galvanometer whose sensibility was 2.1×10^{-10} amperes per millimeter deflection on the three meters distant galvanometer scale. The cell was connected in series with the dry cells, a key, the galvanometer and a 10,000-ohm resistance to protect the latter.

The cell constant of the conductivity cell was determined at 25° with a 0.02 N potassium chloride solution. Using Kohlrausch's value of 2.768×10^{-3} for its specific conductance, six determinations gave a cell constant of $2.19 \times 10^{-2} \pm 0.3\%$. The resistances were all measured at $-78.5'$ using a bath of ether and solid carbon dioxide in a Dewar flask.

TABLE I

RESISTANCE OF LIQUID HYDROGEN SULFIDE

Voltage	Deflection	R X 10 ^{8}	Deflection	R X 10^{-8}	Deflection	$R \times 10^{-8}$
1 5			15	4 76	15	4.76
1 52	16	4 53				
3 00	25	5 71	26	5 49	25	5.71
4 5					36	5.95
5 8	48	5 75				
6 0			49	5 83	47	6.08
9 0			73	5 87	70	6.12
11 8	96 (unsteady)	5 83				
12 0	Unsteady					
19 25	Rose slowly					
Av. value for R		5 33 X 10^8		5 49 $\times 10^8$		5.72×10^8
Av. value for sp cond		4 11 X 10^{-11}		3 99 X 10^{-11}		3.83×10^{-11}

As would be expected, if polarization takes place, the resistance becomes greater at the higher voltages and this is shown by the data. Although there is a gradual increase as the voltage rises, beyond three volts this increase is much less and if an average of the values beyond that point is taken the resistance is 5.87×10^8 and the specific conductance for liquid hydrogen sulfide at $-78.5'$ is 3.78×10^{-11}.

In one of the earliest runs it was observed that the resistances obtained were uniformly high and an examination of the cell showed crystals which were like those formed when water is present in liquid hydrogen sulfide at that low temperature. In order to find the effect of water on the resistance of liquid hydrogen sulfide, three runs were made, in one of which a mere trace of water was added, in the second about 1% and in the third 5%. Table II shows the results.

TABLE II

EFFECT OF WATER ON THE RESISTANCE OF HYDROGEN SULFIDE

Voltage	Galvanometer readings Dry	 Trace H_2O	 1% H_2O	 5% H_2O
1.5	15	12	11	8
3.0	28	20	19	13
6.0	49	34	33	25
9.0	73	52	53	38

Conclusions

1. The specific conductance of liquid hydrogen sulfide determined at $-78.5°$ is 3.7×10^{-11} reciprocal ohms.
2. The presence of even small amounts of water increases the resistance a great deal.

AMES, IOWA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE STATE OF DISPERSION OF CELLULOSE IN CUPRAMMONIUM SOLVENT AS DETERMINED BY ULTRACENTRIFUGE METHODS

BY ALFRED J. STAMM[1]

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Very little is known about the state of dispersion of cellulose in cellulose solvents because hitherto there have been lacking adequate methods for determining the particle size or the molecular weight of coarsely dispersed materials. The usual osmotic pressure methods for determining the molecular weight of solutes of high molecular weight are of little value here, because of the high electrolyte content of the solvents. Even in the case of cellulose derivatives in organic solvents, this method is questionable, because the derivatives themselves cannot be sufficiently purified.

The diffusion experiments of Herzog and Krüger[2] furnish the only available information on the nature of cellulose dispersions in cellulose solvents. Applying Einstein's diffusion law these investigators have calculated the average particle size. Unfortunately, they did not carry their diffusion experiments to low enough concentrations to be sure that they were dealing with free diffusion, and their method of taking only a few samples for analy-

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[1] Fellow of the Rockefeller Foundation. Chemist on leave from the U. S. Forest Products Laboratory, Madison, Wisconsin.

[2] (a) Herzog, *Pulp and Paper Mag. Can.*, 24, 699 (1926); (b) Herzog and Krüger, *Kolloid-Z.*, 39, 250 (1926); (c) *J. Phys. Chem.*, 33, 179 (1929).

sis was not adequate for definitely proving the constancy of their calculated diffusion constant, which is a criterion of a monodisperse system. Herzog and Krüger's work, though of considerable interest, comes far from properly characterizing the cellulose solutions.

It appeared to the author that the ultracentrifuge methods developed by Professor Svedberg in this Laboratory, and so successfully applied in the study of protein solutions, would furnish just the tool necessary for quantitatively studying the nature of cellulose dispersions. It was with the hope of thus furthering the knowledge of cellulose solutions that this research was undertaken.

The Ultracentrifuge

Sedimentation Velocity Method.—In the study of the sedimentation velocity the oil turbine centrifuge capable of developing centrifugal forces from 8000 up to 110,000 times the force of gravity was used.[3] The solution to be studied is placed in a 5° sector shaped cell 12 mm. thick with quartz windows on the two opposite faces. This cell with its steel collar and appropriate fittings is clamped into a drilled slot in the disk-shaped rotor (15 cm. in diameter and 6 cm. thick) of the centrifuge in such a way that the cell windows are parallel to the faces of the rotor. The rotor case is provided with shutter windows so that the dispersed system in the cell can be illuminated and photographed while the centrifuge is in motion. Further details as to the drive, balance and temperature control of the centrifuge, which are of extreme importance, can be found in detail in the other publications.[3]

The rate of settling of the dispersed material is followed photographically during the course of the centrifuging either by the old method of recording the changes in light absorption, or the new method, to be described more fully later, of following the changes of the index of refraction of the sedimenting system. From the change of the position of the sedimentation boundary with time the specific sedimentation velocity of the settling material can be calculated according to the equation

$$s = \frac{1}{\omega^2 x} \times \frac{dx}{dt} \qquad (1)$$

where ω is the angular velocity of the centrifuge, x is the distance from the axis of rotation to the sedimentation boundary, and t is the time. The diffusion constant D can also be determined for a monodisperse material from the extent of spreading of the sedimentation boundary with time. From these two quantities, s and D, together with V, the partial specific volume of the sedimenting material, and ρ, the density of the solvent, the molecular weight of the sedimenting material can be calculated independently of Stokes' law of settling, thus

$$M = \frac{RTs}{D(1 - V\rho)} \qquad (2)$$

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[3] (a) Svedberg and Nichols, THIS JOURNAL, 49, 2920 (1927); (b) Svedberg, *Z. physik. Chem.*, 127, 51 (1927); (c) "Colloid Chemistry," The Chemical Catalog Co., Inc., New York, 1928, 2d ed., pp. 146–167.

where R is the gas constant and T the absolute temperature, by merely assuming the equality of the frictional forces that determine both s and D.

Determination of Concentration Gradients in **the** Sedimenting Systems.—The concentration gradients in the cellulose solutions cannot be determined by the ordinary light absorption method, which has been used in the study of all of the proteins, because cellulose, like other carbohydrates,[4] shows no light absorption even in the short wave length ultraviolet. For this reason a new method, developed by Ole Lamm in this Laboratory, was used and found to be satisfactory. Lamm's method[5] consists in determining the changes in the concentration gradient by following the changes in the index of refraction of the dispersed system. This is done by photographing a small uniform transparent scale which is mounted in the centrifuge casing behind the cell. The light from the scale in passing through the cell is refracted differently in passing through the different concentrations along the length of the sedimenting system. This differential bending of the light causes a distorted image of the scale, as is indicated in Fig. 1.

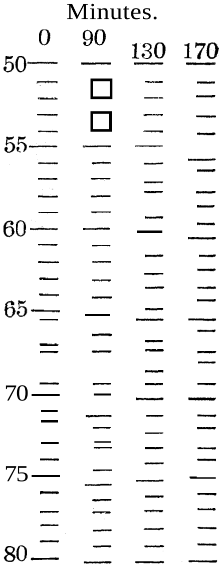

Fig. 1.—Diagrammatic representation of the photographs of the scale for a typical sedimentation velocity run on a 0.10% solution of cotton linters α-cellulose.

The mathematics of the method are so completely developed by Lamm[5] that no attempt will be made to duplicate it here. The fundamental equation on which the measurements are based

$$Z = Gab\frac{dn}{dx} = f\frac{dc}{dx} \qquad (3)$$

gives the relationship between the photographic scale displacement Z and the rate of change of the index of refraction n with changes in height, x. G is the photographic enlargement, a the thickness of the sedimenting layer in the cell and b the optical distance between the scale and the center of the cell. The photographic scale displacement Z is further proportional to the rate of change of the concentration c with changes of the height x, when the refractive index is a linear function of the concentration.

The scale used in this research had one hundred divisions 0.0201 cm. apart; *a* was in all cases 1.2 cm., *b* was either 10.2 or 12.4 cm. and for one run it was **25.2** cm., *G* was 0.473 when *b* was 10.2 cm., 1 the optical distance between scale and the lens was 302 cm. when *b* was 10.2 cm.

The mercury vapor lamp used in the protein researches[3] was used for illumination. The city current instead of the storage batteries was used as the source of current. as great constancy of the light intensity is *not* needed for this method, as *is* the case with

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[4] Kwiecinski and Marchlewski, Bull. *intern. acad. Polonaise,* [A] 271 (1928).

[5] Lamm, *Z. physik Chem.,* (a) 138,313 (1928); (b) 143, 177 (1929).

the light absorption method. The cuprammonium solution served as its own filter, the **435 mμ** wave length line being the only intense wave length emitted from the lamp that was not absorbed by the cellulose solvent.

The lens used was a Zeiss F/12.5 lens with a 100-cm. focal length. Diaphragm stops F/44, F/61 and F/88 were used, F/44 when the concentration gradients were small, just at the start and at the end of the runs and F/61 and F/88 for moderate and steep concentration gradients, respectively. In many cases pictures were taken with all three stops, and only the sharpest were used for the measurements. Imperial Process plates, 9 × 12 cm., were used for the exposures; 36 exposures could be taken on each plate. The times of exposure used for the stops F/44, F/61 and F/88 were 7.5 sec., 15 sec. and 30 sec., respectively. The plates were developed for two minutes in hydroquinone–potassium metabisulfite hard developer.

A micro comparator made in this Laboratory using a Johansson screw (Eskilstuna, Sweden) was used for measuring the displacement of the lines on the photographic plates. A Leitz No. 3 objective and a No. 2 ocular giving a magnification of 60 times were used for reading. The comparator drum could be read to 0.0001 cm. and check settings could usually be made to 0.0002 cm. A careful examination of the screw showed it to be accurate to 0.0001 cm.

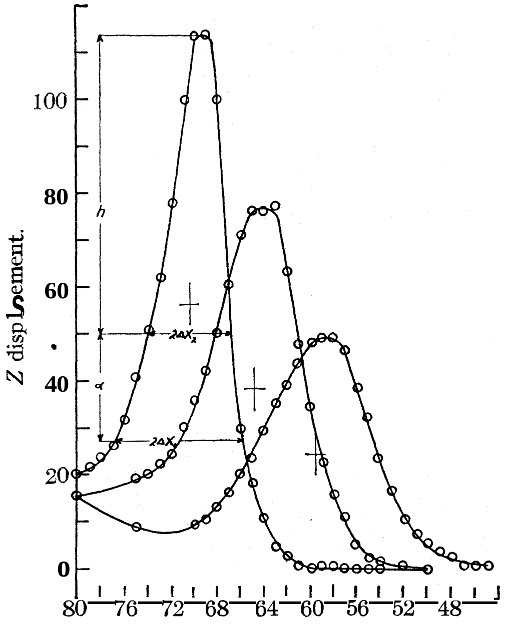

Fig. 2.—Photographic scale displacements for a typical sedimentation velocity run on a 0.10% solution of cotton linters α-cellulose.

Calculation of the Specific Sedimentation Velocity.—In Fig. 2 the photographic scale displacements Z in thousandths of a mm. are plotted against the scale division numbers for the enlarged representation of the photographic image shown in Fig. 1. That is, the rate of change of concentration with height in the sedimenting system is plotted against the height. The positions of the maxima in these first derivative of concentration curves correspond to the inflection points in the simple concentration curves obtained by the light absorption method, which, in turn, corresponds to the photographic position of the sedimenting boundary. The Δx values from the curves, distances between the maxima, or better, the vertical bisectors of the areas of the curves for two successive exposures taken Δt time apart, have to be corrected to the basis of actual cell distances by multiplying by the actual distance between scale divisions, 0.0201 cm., and by the factor $(1 - b)/l$ to change from scale distances to distances in the cell. There is also a slight shift in x position due to the curvature of a light beam in passing through the solution. This curvature varies directly with the steepness of the concentration gradient at the point under consideration. The correction for the position of the sedimentation boundary is $-\Delta Z_{\text{max.}}/2G$ in the direction of increasing concentration when the sedimentation is calculated from a point at half the height of the vertical bisector. The absolute corrected distance between the maxima on two successive exposures, $\Delta X_{\text{corr.}}$ is thus

$$\Delta X_{\text{corr.}} = \frac{l - b}{l}\left(0.0201\,\Delta x - \frac{\Delta Z_{\text{max.}}}{2G}\right) \tag{4}$$

where Δx is in scale division units. The sign of the correction is plus as Z decreases with increasing time.

As the exact position on the scale corresponding to the position of the meniscus of the solution in the cell cannot be directly determined from the photographs, the distance from the center of rotation to the sedimenting boundary has to be determined in a roundabout way. From the average value of $\Delta X_{\text{corr.}}/\Delta t$, and the time elapsed up to the first exposure, the position of the sedimenting boundary at zero time, which corresponds to the position of the meniscus of the solution, can be calculated. From exposures taken with the camera focused on the cell rather than on the scale, the exact height of the solution in the cell can be measured with the comparator. Knowing the distance from the center of rotation to the bottom of the cell, the distance from the center of rotation to the sedimenting boundary can be calculated. The specific sedimentation velocity can then be calculated using Equation 1.

Calculation of the Diffusion Constant.—The diffusion constant can be calculated for a monodisperse system from the extent of spreading of the sedimentation boundary with changes in the time, that is, from the breadth of the curves of Fig. 2. If there were no diffusion taking place at the sedimentation boundary the concentration gradient would be infinite right at the boundary and zero to each side. The sedimentation curve would then be represented by a straight vertical line.

Only the method of determining D from the curves will be given here. For the theoretical considerations and the development of the equations the reader is referred to Lamm's publication.[5b] Let $2\Delta x_1$ represent the breadth of the curve at any height and $2\Delta x_2$ the breadth of the curve at such a height that $\Delta x_1^2 = 2\Delta x_2^2$. Let α represent the Z distance between the x_1 and the x_2 lines, and h the Z distance from the x_2 line to $Z_{\text{max.}}$ as indicated in Fig. 2. Then the diffusion constant

$$D = \frac{0.1086\,\Delta x_2^2}{t\log_{10}(h/\alpha)} \tag{5}$$

where t is the diffusion time. The value of Δx_2 determined from the curves must be corrected to absolute units and from the scale to the cell position as before by multiplying by 0.0201 and $(l - b)/l$.

Materials **Used.**—Cuprammonium solution was chosen for the cellulose solvent as chemical studies have shown that it is the nearest approach to a true physical solvent of all of the cellulose solvents. Further it is of considerable importance because of the cuprammonium artificial silk industry, and because this is the chief solvent used for viscosity comparisons of different grades of cellulose.

The cuprammonium solution was prepared by drawing carbon dioxide-free air slowly through a tall cylinder containing concentrated ammonia (sp. gr. 0.91) and strips of electrolytic copper foil for from six to eight hours. A large stock solution was prepared for all of this work, and kept in a tightly stoppered bottle in the dark. The copper concentration was determined by evaporation of 2-cc. portions, igniting and weighing as the oxide. The ammonia concentration was determined by titrating a diluted portion against 0.1 N hydrochloric acid using methyl orange as an indicator. The stock solution contained 1.28% of copper and 22.0% of ammonia.

All of the measurements reported in this paper were made on a cotton linters α-cellulose. The a-cellulose content was 99.6%, the copper number 0.17 (Braidy method) and the ash 0.031%.

A heavier lubricating oil, Vacuum Oil Co., Mobile B, was used as a seal over the surface of the cuprammonium solution in the centrifuge cell than was used in the protein researches, as greater precautions against evaporation are necessary here on account of the high vapor pressure of the ammonia. Careful examination showed that no ammonia evaporated through the oil layer.

Experimental

The new index of refraction method of measuring the concentration gradients, and the accompanying method of calculating the specific sedimentation velocity and diffusion constant have been tested by making runs on a number of proteins by this method and by the old light absorption method by both Lamm[5b] and the author.[6] The agreement was found to be quite satisfactory.

Specific Volume.—The partial specific volume of the pure cotton linters a-cellulose was determined pycnometrically at 19.8°. Measurements were made at three different concentrations in two different solvents, as shown in Table I.

TABLE I

PARTIAL SPECIFIC VOLUME OF COTTON LINTERS a-CELLULOSE IN CUPRAMMONIUM SOLVENT OF DIFFERENT CONCENTRATIONS AT 19.8°

Cellulose concn., %	Solvent concn. Cu, %	Solvent concn. NH_3, %	V
0.568	1.28	22.0	0.645
.764	0.83	16.2	.637
1.029	1.28	22.0	.643

The values for the specific volume are constant within experimental accuracy, which unfortunately is not as great as might be desired due to

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[6] Svedberg and Stamm, THIS JOURNAL, 51, 2170 (1929).

the high vapor pressure of the solvent The results show, however, that the specific volume is not affected to any appreciable extent by the cellulose concentration or the concentration of the solvent.

Preparation of Cellulose **Solutions.**—The cellulose solutions were made up in small glass-stoppered vials of 8-cc. total capacity by pipetting 5 cc. of the solvent into the vial, dropping in the weighed cellulose sample, and immediately stoppering, then gently rotating until the cellulose was dissolved. By this method the sample was not prepared entirely free from oxygen, so for comparison a few samples were made up by first warming the solvent to 60° in the vial, opening for one-half minute for the air to be displaced by the ammonia, which has a vapor pressure of **2.5** atm. at this temperature, then dropping in the weighed cellulose sample, stoppering and holding at the elevated temperature for fifteen minutes. After standing at room temperature for the length of time indicated, a sample was quickly pipetted into the centrifuge cell and sealed with a layer of lubricating oil.

Colloidal Nature of Solvent.—A run was made on the pure cuprammonium solvent to determine if it contained any sedimentable material. The results showed the presence of some polydisperse material, which is most likely colloidal copper hydroxide.[7] The sedimentation velocity ranged from 5×10^{-12} cm./sec. per cm./sec.^{2} to 10 to 100 times this value. The particles thus range in size from 6.5 mμ in diameter to more than **20.0** mμ, using Stokes' law for the calculations and taking the density of copper hydroxide as **3.37.** Unfortunately the percentage of the total copper concentration that is colloidally dispersed cannot be determined definitely without knowledge of the relationship existing between the sol concentration and the refractive index. It is very likely less than 10% of the total copper concentration, however.

The sedimentation velocity of this colloidal copper hydroxide is fortunately 10 to 100 times greater than that of the cellulose so its presence does not interfere with the work of the present investigation. It is merely necessary to avoid making measurements near the bottom of the cell where this material becomes concentrated.

Sedimentation Velocity Results

Table II gives the results of a typical sedimentation velocity run made on a 0.10% cellulose solution. The data for the first three exposures are given in Fig. 1, and the diagrammatic representation thereof in Fig. 2. The table shows not only a constant value for the sedimentation velocity but also for the diffusion constant, indicating that the material under investigation is monodisperse. This is further indicated by the general symmetry of the curves of Fig. 2. The slight deviation from symmetry

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[7] Bhatnagar, Goyle and Prasad, *Kolloid-Z.*, 44, 79 (1928).

at the extreme left, which is caused by a slight displacement near the meniscus of the solution, indicates the presence of relatively small amounts of a material of a much finer state of dispersion. This effect was in all cases very small for the runs made on pure cotton linters α-cellulose.

TABLE II

RESULTS OF A TYPICAL SEDIMENTATION VELOCITY RUN MADE UPON A 0.10% SOLUTION OF COTTON LINTERS α-CELLULOSE

Copper concn. of solvent, 0.64%; NH_3 concn. of solvent, 22.0%; V = 0.642; p = 0.9356; rel. visc. of solvent, 1.365; age of solution at time of starting run, 0.5 hr.; length of column of solution, 1.16 cm.; thickness of column, 1.20 cm.; average speed, 44,900 r. p. m.; time interval between exposures, 40 min.; average temperature, 20.7".

Sedimentation

AX, scale div.	$\frac{\Delta Z_{\text{max.}}}{2G}$, cm.	$\Delta X_{\text{corr.}}$, cm.	X mean, cm.	ω^2 X 10–7	s_{20} cm./sec. per cm./sec. X 10^{13}
5.7	0.0038	0.1136	4.91	2.22	4.29
5.5	.0029	.1088	5.01	2.21	4.03
6.0	.0015	.1174	5.12	2.20	4.28
				Av.	4.20

Diffusion

Time, sec.	$2\Delta X_2$, scale div.	$\Delta(X_{2\text{corr.}})^2$, cm.^{2}	h, cm. × 10^3	α, cm. × 10^3	D_{20}, cm.^{2}/sec. X 107
5,160	7.7	0.00552	6.35	2.30	2.58
5,160	6.4	.00381	5.10	2.45	2.48
7,560	8.5	.00672	3.40	1.60	2.88
7,560	7.2	.00482	2.65	1.50	2.75
9,960	11.2	.01165	2.75	1.05	2.98
9,960	9.0	.00752	2.00	1.05	2.87
12,360	11.5	.01230	1.40	0.60	2.89
				Av.	2.77

Table III gives a summary of all of the sedimentation velocity runs. Part A shows the effect of varying the concentration of the solvent. For the purpose of comparison both the specific sedimentation velocity and the diffusion constant have been corrected to the basis of sedimentation and diffusion in the most concentrated solvent. The specific sedimentation velocity depends inversely upon the viscosity of the solvent, and directly upon the difference in density between that of the particle and of the solvent, and the diffusion depends inversely upon the viscosity of the solvent. The results show that the specific sedimentation velocity is practically independent of the copper and of the ammonia concentration over the range tested. The diffusion constant is also unaffected by the changes in copper concentration, but it is affected by appreciable reductions in the ammonia concentration. This latter may be due to an increased gel tendency.

Part B of Table III gives the effect of varying the cellulose concentration for solutions one-half and sixteen hours old, respectively. In each case

TABLE III

SUMMARY OF RUNS MADE ON COTTON LINTERS α-CELLULOSE

A. Effect of Varying the Solvent Concentration, Cellulose Concn. 0.10%. Age of Solutions at Time of Starting Runs, 0.5 hr.

No.	Solvent Cu, %	Concn. NH_3, %	Density of solvent	Rel. visc. of solvent	Av. r. p. m.	s_{20}, cm./sec. per cm./sec. $\times 10^{13}$	D_{20} cm.^{2}/sec. $\times 10^7$	Basis of concn. Solvent s_{20} $\times 10^{13}$	D_{20} $\times 10^7$
1	0.32	22.0	0.9297	1.350	44,800	4.27	2.80	4.03	2.72
2	0.64	22.0	.9356	1.365	44,900	4.20	2.77	4.05	2.72
3	1.28	22.0	.9474	1.390	43,400	4.18	2.68	4.18	2.68
4	1.28	22.0	.9474	1.390	36,000	4.29	2.79	4.29	2.79
5	1.28	18.4	.9583	1.330	42,700	4.28	2.63	4.17	2.52
6	1.28	14.8	.9692	1.275	45,000	4.23	1.76	4.03	1.62

B. Effect of Varying the Cellulose Concentration and the Age of the Solution. Solvent Concn., 1.28% Cu, 22.0% NH_3

No.	Cellulose concn., %	Age of soln., hours	Av. r. p. m.	s_{20}, cm./sec. per cm./sec.^{2} $\times 10^{13}$	D_{20}, cm.^{2}/sec. $\times 10^7$
1	0.50	0.5	41,900	2.31	0.237
2	.20	0.5	44,800	3.72	0.540
3	.10	0.5	43,400	4.18	2.68
4	.10	0.5	36,000	4.29	2.79
5	.05	0.5	45,000	4.38	4.52
6	.025	0.5	42,800	4.32	5.15
7	.50	16.0	42,800	2.56	0.640
8	.50	16.0	42,900	2.47	.673
9	.20	16.0	43,100	3.41	2.14
10	.12	16.0	43,100	3.99	3.51
11	.10	16.0	43,200	3.95	4.07
12	.07	16.0	43,100	4.18	5.10
13	.05	16.0	43,100	3.92	5.58
14	.025	16.0	43,200	3.65	5.90
15	.10	7 days	45,100	4.28	4.00
16	.10	0.5	45,200	4.26	2.77[a]
17	.10	16.0	43,000	4.24	2.73[a]
18	.10	0.5	43,000	4.43	1.27[b]

[a] Heated to 60°. [b] Added 0.10% glucose.

the specific sedimentation velocities increase slightly with a decrease in concentration in a linear manner as is indicated in Fig. 3. The deviation between the two lines is practically within the range of experimental error. The diffusion constants, on the other hand, increase at a greater rate with a decrease in concentration, and the values from the fresh solutions are considerably smaller than for the solutions sixteen hours old.

This slight increase in the sedimentation velocity and a relatively large increase in the diffusion constant with a decrease in concentration has also been obtained by Svedberg and Chirnoaga[8] for the protein, hemocyanin from *Helix pomatia*. The protein has a molecular weight of 5,000,000. The molecules are approximately spherical with a diameter of about 24 mμ. The diffusion constant for a 3% solution of this protein is approximately

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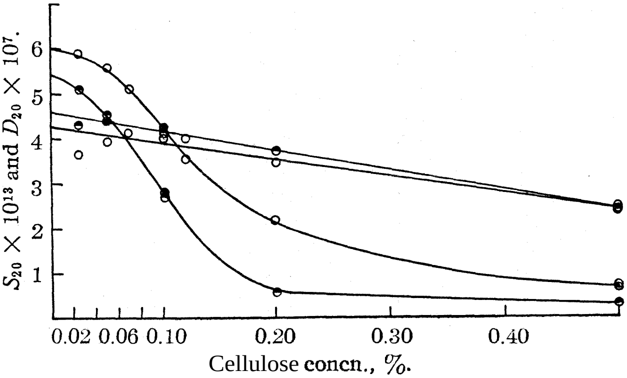
[8] Svedberg and Chirnoaga, THIS JOURNAL, 50, 1407 (1928).

one-third of its value for an infinitesimal concentration. The calculated average distance between the surface of adjacent molecules in the 3% solution is only about one and a half times the molecular diameter. The proximity of the molecules to each other for this concentration is very likely the cause of the low diffusion constant, the intermolecular action appreciably hindering free diffusion.

In the case of the 0.5% cellulose solutions the diffusion constant differs from the value for free diffusion by a still greater amount than in the case of the 3% solution of the hemocyanin, thus indicating that the intermolecular action must be still greater. The concentration effect in this case is very likely due to the rod shape of the molecules rather than their mass. From measurements of the width of the x-ray diffraction bands, Mark and Meyer[9] have estimated the length of the cellulose molecule or micelle in the solid crystal lattice to be 50 mμ. If the molecules in solution are of this same order of length, the marked decrease in the diffusion constant can well be accounted for on the basis of the intermolecular forces which come into play when any part of one molecule comes within the range of action of another. Sedimentation, on the other hand, involves directed motion and should be affected far less by concentration changes, as is the case.



◓, Solutions 0.5 hour old; ○, solutions 16 hours old.

Fig. 3.—Variation of the specific sedimentation velocity and of the diffusion constant with cellulose concentration.

Degradation of Solutions by the Oxygen of the Air.—The increase of the diffusion constant with an increase of the age of the solution (see Table IIIB) is worthy of a closer examination. Is the effect due to the inherent aging of the solution or to a chemical change caused by the slight amount of oxygen present? The following viscosity measurements (see Table IV) give some insight into this matter. A solution was prepared

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[9] Mark and Meyer, *Z. physik.* Chem., 2B, 115 (1929).

containing 0.050 g. of cellulose in 50 cc. of cuprammonium solvent (1.28% Cu and 22.0% NH_3). Portions of 5 cc. each were quickly pipetted into the 8-cc. vials. The vials were immediately stoppered and allowed to stand for various lengths of time at room temperature (approximately 18"). Sample 6 was opened to the air for two hours the day before the determinations were made. Sample 7 was kept in the big bottle in contact with a large volume of air. Samples 8 and 9 were prepared by the previously mentioned technique for exclusion of oxygen of the air. The viscosity determinations were made in a 53-second Ostwald viscosimeter at 19.8". The table shows that exclusion of the oxygen of the air prevents a change in the viscosity of the solution with time. The small amount of air ordinarily present in the vials, where no precautions for its exclusion were taken, shows a definite effect upon the viscosity. The presence of oxygen causes a decrease in the viscosity of the solution with time. Presumably when the oxygen is used up the viscosity remains constant. Allowing more oxygen to enter the vial, however, causes a further reduction in viscosity. Sedimentation velocity measurements (Nos. 16 and 17, Table IIIB) further show that exclusion of the oxygen of the air also prevents a change of the sedimentation velocity and of the diffusion constant with time. The previously observed change, therefore, must be due to the effect of the oxygen of the air on the solution and not to any inherent aging of the solution.

TABLE IV

EFFECT OF THE AGE OF 0.10% CELLULOSE SOLUTIONS IN CUPRAMMONIUM SOLVENT (1.28% CU, 22.0% NH_3) ON THE VISCOSITY OF THE SOLUTION

No.	Age of soln., hours	Viscosity relative to H_2O at 19.8"	Remarks
	....	1.39	Of solvent
1	1.5	2.12	Access to O_2 in vial
2	18.5	1.95	Access to O_2 in vial
3	43.0	1.94	Access to O_2 in vial
4	121.0	1.91	Access to O_2 in vial
5	309.0	1.91	Access to O_2 in vial
6	309.0	1.66	Opened to air for 2 hrs.
7	309.0	1.58	Access to large volume of O_2
8	0.5	2.13	O_2 free
9	16.0	2.14	O_2 free

A run was made on a solution twenty-two days old that had been kept in a big bottle with a large volume of air to act on the sample. The solution was so completely decomposed that with the highest centrifugal force obtainable no maximum in the *Z* displacement could be obtained though a *Z* displacement near the meniscus was quite evident. This shows that the dispersion of the degraded cellulose was so fine that it could not be studied with the centrifugal forces available, but part of it at least was still much coarser than the simple glucose units.

From the results of the above run, where the large volume of air present caused a breaking down of the cellulose particles, it seems quite probable that a similar effect has resulted in the case of the sixteen-hour old solutions only to a much smaller extent. The degradation has made itself noticeable to a very slight extent in the case of the sedimentation velocity, but quite appreciably in the case of the diffusion constant. Such a slight decrease in the sedimentation velocity and a more appreciable increase in the diffusion constant can be caused by the presence of small percentages of a material of a somewhat finer state of dispersion. The fact that the diffusion constant does not increase from exposure to exposure in a single run, however, indicates that the material cannot be appreciably heterodisperse.

A run was made on a 0.10% cellulose solution to which 0.10% glucose had been added (see Table IIIB). The sedimentation velocity was normal, but the diffusion constant was quite low. The viscosity of the solvent was increased by only a fraction of a per cent. by the addition of the glucose, so this cannot account for the reduction of the diffusion constant. The viscosity of the solution, however, was considerably higher than that of a 0.10% cellulose solution without the glucose present (2.49 rel. visc. instead of 2.12). The decreased diffusion constant must then be due to an increased gel tendency caused by the presence of the glucose.

Molecular Weight of the Dispersed Cellulose.—From an extrapolation of the curves of Fig. **3** for the change of the sedimentation velocity and of the diffusion constant with concentration, the ideal sedimentation velocity and diffusion constant for an infinitesimal concentration can be obtained. For the undegraded solutions $s_{20} = 4.6 \pm 0.2 \times 10^{-13}$ and $D_{20} = 5.4 \pm 0.5 \times 10^{-7}$. Using the average value of V = 0.642 and p = 0.947, then according to Equation 2, M = 53,000 ± 7000.

The above value for the molecular weight is, of course, the molecular weight of the cellulose cuprammonium complex, whether it is a definite stoichiometric combination of 1 Cu:1$C_6H_{10}O_5$ according to Hess[10] or whether the copper complex is merely absorbed according to Bauer.[11] In the case of the stoichiometric combination, the copper content would be 28.0%. From Bauer's adsorption isotherm $X/m = 0.386$ g. of copper per g. of cellulose for the solvent containing 1.28% copper and $X/m = 0.260$ g., for the solvent containing 0.32% copper. The ratio of the molecular weights in the two solvents would be 1.10, and the ratio of the sedimentation velocities 1.065, as $s_1/s_2 = (M_1/M_2)^{2/3}$. The experimental ratio is 1.04. The deviation is well within the range of experimental error. In the case of the solvent containing 1.28% copper, the complex contains

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[10] **Hess, *Ann.*, 435, 1–144 (1923);** *Z. angew Chem., 37, 993 (1924); Kolloid-Z.*, 36, 260 **(1925).**

[11] *Bauer, Kolloid-Z.*, 36, **257 (1925).**

27.8% copper, which is practically the same as Hess's value for a stoichiometric combination. On either basis, then, the molecular weight of the uncombined cellulose would be 38,000 ± 5000.[12] The dispersed cellulose particles must then be made up of from 200 to 260 of the simple $C_6H_{10}O_6$ units.

It is of interest to compare the molecular weight of the cellulose–copper complex with that calculated from Herzog and Krüger's diffusion results for cuprammonium solutions.[2b] Applying Einstein's diffusion equation

$$D = \frac{RT}{N} \times \frac{1}{6\eta\pi r} \tag{6}$$

the average radius of the cellulose particle is found to be 5.0×10^{-7} cm. Using the expression for the molecular weight

$$M = \frac{4}{3}\pi r^3 \rho_p N \tag{7}$$

where r is the radius of the particle, ρ_p, the density of the particle, and N, Avogadro's number, M is found to be 495,000, which is just about ten times the value reported in this paper. The discrepancy seems to be due to the fact that Herzog and Krüger did not extend their diffusion measurements to sufficiently low concentrations to get entirely free diffusion. Their investigation also involves the assumption that the particles are spherical, which is most likely far from the truth.

Sedimentation Equilibrium Method.—Two runs were made on the cellulose solutions using the sedimentation equilibrium method so as to determine the molecular weight of the dispersed cellulose independently of measuring the sedimentation velocity and the diffusion constant. With this method a centrifugal force of only sufficient magnitude is applied to give a readily measurable constant concentration gradient after a reasonable duration of time that represents the attainment of equilibrium between the backward diffusion of the dispersed material and the outward sedimentation. The molecular weight is given by the relation[13,3c]

$$M = \frac{2RT \ln (c_2/c_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)} \tag{8}$$

where c_1 and c_2 are the concentrations at the distances x_1 and x_2 from the center of rotation, and the other symbols have the same significance as previously. The index of refraction method, however, does not give the concentrations directly, but rather a function which is proportional to the rate of change of concentration with height. A mathematical analysis by Lamm has shown the following relationship to be valid

[12] Mark and Meyer, *Z. physik. Chem.*, [Abt. B] 2, 115–45 (1929). These investigators have determined the approximate molecular weight of cellulose in the fiber form from the width of the x-ray diffraction lines obtained in their crystallographic studies. M = 10^5 to 10^6. This is in fair agreement with the above results.

[13] (a) Svedberg and Fåhraeus, THIS JOURNAL, 48, 430 (1926); (b) Svedberg and Nichols, *ibid.*, 48, 3081 (1926).

$$\frac{c_2}{c_1} = \frac{(\mathrm{d}n/\mathrm{d}x)_2\, x_1}{x_2\, (\mathrm{d}n/\mathrm{d}x)_1} = \frac{Z_2\, x_1}{Z_1\, x_2} \tag{9}$$

Applying this relationship in Equation 8 for the concentration ratio, the molecular weight can be readily calculated by merely measuring the Z displacements for two different heights in the equilibrium system. The x values have to be corrected, as previously described, for the slight bending of a light beam in passing through the solution $\Delta Z/G$, and for the change from scale distances to cell distances $(1 - b)/l$.

The measurements were made in the new low speed centrifuge (2000 to 12,000 r. p. m.) driven by a Siemens–Schuckert motor generator set. The centrifuge is completely described in a recent publication from this Laboratory.[14] The scale was mounted in an adjustable tubular holder placed between the prism and the shutter. A horizontal reference cross hair was mounted across the outside face of one of the cell windows. From the shadow cast by this line on the photographic image of the scale, and from its actual position with respect to the bottom of the cell, the point in the cell corresponding to any of the scale divisions can be definitely determined.

A preliminary run was first made with only the cuprammonium solvent in the solution cell and in the standard cell. The scale divisions became quite regular after several hours, except near the bottom of the cell. This shows that the colloidal copper hydroxide is completely removed even at this lower speed. The exact distance from one of the lines that was superimposed on the standard cell image to each of the scale division lines, that were superimposed on the solution cell image, was determined. Runs were then made with the cellulose solution in the solution cell. The exact distance of each of the lines from the same reference line was again determined, and the Z values were calculated from the differences. This method of determining the Z displacements proved to be far more accurate than that used in the first part of this research.

The results of one of the equilibrium runs made on a 0.50% cellulose solution are given in Table V. The molecular weight values obtained at the different heights are quite uniform, again showing that the cellulose is monodisperse. This run required one hundred and sixty hours for the system to come to equilibrium. The time is considerably greater than that required in the study of any of the proteins.[3c,13] This is due to the high viscosity or gelation of the solution, which manifested itself in the sedimentation velocity study by giving abnormally low diffusion constants in solutions of this concentration.

A run made on a 0.20% cellulose solution took less than seventy-two hours to come to equilibrium. This run was made at a speed of 8350 r. p. m., and gave an average molecular weight of 54,400.

These results are in very good agreement with those obtained in the sedi-

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[14] Svedberg and Sjögren, THIS JOURNAL, **51, 3594 (1929).**

TABLE V

RESULTS OF A TYPICAL EQUILIBRIUM RUN ON COTTON LINTERS α-CELLULOSE

Concentration, 0.50% cellulose; solvent, 1.28% Cu and 22.0% NH_3; $V = 0.642$; $\rho = 0.947$; length of column of solution, 0.63 cm.; thickness of column, 0.4 cm.; distance of outer end of solution from axis of rotation, 5.95 cm.; distance from scale to center of cell, 20.0 cm.; distance between scale divisions, 0.0257 cm.; optical distance between scale and photographic lens, 227.0 cm.; time of exposure, 1 min.; time of centrifuging, 190 hrs.; average speed, 7750 r. p. m.

Distance from center of rotation, cm. X_2	X_1	Photographic scale, displacement in cm. Z_2	Z_1	Ratio of concns., C_2/C_1	Mol. wt.
5.35	5.30	0.00685	0.00573	1.185	58,400
5.40	5.35	.00820	.00685	1.187	58,200
5.45	5.40	.00983	.00820	1.188	58,100
5.50	5.45	.01185	.00983	1.194	59,600
5.55	5.50	.01435	.01185	1.199	60,200
5.60	5.55	.01730	.01435	1.194	58,400
5.65	5.60	.02080	.01730	1.192	57,200
				Mean	58,600

mentation velocity study, and the two taken together quite definitely characterize the nature of the dispersion of pure cellulose in cuprammonium solvent.

Note on Viscose Solutions.—The author was anxious to compare cellulose dissolved in other solvents with the above results, but time was available for only one such run. This was made on a **0.26%** viscose solution in 2.2% sodium hydroxide. The viscose was prepared from the above cotton linters a-cellulose. The relative viscosity of the solution was **2.17.** The curves were symmetrical with but one maximum, thus indicating that the system is monodisperse. The sedimentation velocity, $s_{20} = 2.8 \times 10^{-13}$ cm./sec. per cm./sec.^{2} and the diffusion constant, $D_{20} = 0.71 \times 10^{-7}$ cm.^{2}/sec. Converted to a basis of sedimentation and diffusion in a solvent with the same density and viscosity as the cuprammonium solvent, $s_{20} = \mathbf{3.3} \times 10^{-13}$ and $D_{20} = \mathbf{0.73} \times 10^{-7}$. This sedimentation value is very similar to that for cellulose in the cuprammonium solvent at the same concentration. The diffusion is also of the same order of magnitude as that for the cuprammonium solvent. The molecular weight of the cellulose xanthogenate in the viscose solution must then be very similar to the value given above for the cellulose solutions.

The author wishes to express his sincere thanks to Professor The Svedberg for the use of the ultracentrifuge equipment of this Laboratory, and for the help which he always freely gave toward the carrying out of this research. The author also wishes to thank Mr. Ole Lamm, of this Laboratory, for allowing him to use the newly developed method for determining the concentration gradients, and for the help which he gave in applying this method.

Summary

1. The nature of the dispersion of pure cotton linters a-cellulose in cuprammonium solvent was studied with the aid of the ultracentrifuge.

2. The cellulose is monodisperse and has a molecular weight of **55,000 ± 7000.** On a copper-free basis it is **40,000 ± 5000.** The particles must be made up of from **200** to **260** of the simple $C_6H_{10}O_5$ units.

3. The specific sedimentation velocity of the dispersed cellulose increases slightly with a decrease in concentration while the diffusion constant increases quite appreciably. This is explained on the basis of the gelation of the system.

4. Oxygen of the air is shown to cause a degradation of the solution by decreasing the particle size.

5. The cuprammonium solvent is shown to contain some colloidally dispersed particles. Their sedimentation velocity ranges from ten to several hundred times that of the cellulose particles. Their size ranges from 6.5 mμ in diameter to more than **20.0** mμ.

6. A single run made on a viscose solution indicates that cellulose xanthogenate dissolved in a dilute alkali solution has approximately the same molecular weight as the above cellulose.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

DIFFERENCES BETWEEN THE STATE OF DISPERSION OF ISOLATED WOOD CELLULOSE AND COTTON CELLULOSE IN CUPRAMMONIUM SOLVENT

BY ALFRED J. STAMM[1]

RECEIVED JANUARY 22, 1930 PUBLISHED AUGUST 5, 1930

All of the available chemical evidence indicates that there is a definite difference between isolated wood cellulose (Cross and Bevan cellulose) and cotton cellulose. The presence of mannan and pentosans in the wood cellulose has been shown in many cases, but it has never been found possible to remove these impurities completely. Because of this fact, it has not been possible to determine definitely from chemical evidence whether the hypothetically pure wood cellulose differs from pure cotton cellulose. X-ray studies on the other hand show that wood cellulose and cotton cellulose give the same interference bands and the same axial ratios,[2] thus indicating that the fundamental building units are identical. Although this evidence indicates that the hypothetically pure wood cellulose and the pure cotton

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[1] **Fellow of the Rockefeller Foundation. Chemist on leave from the U. S. Forest Products Laboratory, Madison, Wisconsin.**

[2] Herzog and Jancke, *Z. Physik*, 3, 196 (1920).

cellulose are identical, it does not exclude either the possibility of difference in the degree of association of the fundamental building units or the further possibility of difference in the manner in which these units are put together. The facts should be made evident from a quantitative study of the degree of dispersion of the celluloses dissolved in a cellulose solvent.

The ultracentrifuge technique, developed and applied to the study of pure cotton linters a-cellulose in the previous research,[3] was also used for the study of several different wood celluloses as well as other cotton celluloses.

Materials Used.—The solvent used for all of the measurements was the previous stock cuprammonium solution (1.28% Cu and 22.0% NH_3). Three different forms of cotton cellulose and four of wood cellulose were used. The cotton linters a-cellulose was the same as that studied in the previous research. The α-cellulose content was 99.6%, the copper number 0.17 (Braidy method) and the ash content 0.031%. The absorbent cotton was a long staple, extracted, non-medicated cotton with an a-cellulose content of 99.2%. The filter paper was a high-grade paper made from cotton linters stock that had not been subjected to acid treatment. The a-cellulose content was 97.2%. The aspen cellulose obtained from the wood by the Cross and Bevan method had an a-cellulose content of 71.2%. The white spruce cellulose was obtained by the same method. Unfortunately the sample was not sufficiently large for an a-cellulose determination to be made. The a-cellulose from spruce sulfite pulp was prepared by the Stora Kopparbergs Bergslags Aktiebolag in Falun, Sweden. The α-cellulose content was 96.1%, copper number 0.98 (Braidy method), and ash content 0.08%. The bleached sulfite pulp was an ordinary spruce pulp. The a-cellulose content was 81.4%.

Cotton Cellulose.—Table I gives a comparison of the specific sedimentation velocities and the diffusion constants obtained from runs made

TABLE I

SUMMARY OF RESULTS ON 0.10% SOLUTIONS OF DIFFERENT CELLULOSES DISSOLVED IN CUPRAMMONIUM SOLVENT (1.28% Cu AND 22.0% NH_3) SOLUTIONS ONE-HALF HOUR OLD

Material	a-Cellulose, %	Cu no.	Rel. visc. of soln.	Constituent A $s_{20} \times 10^{13}$	Constituent A $D_{20} \times 10^7$	Constituent B $s_{20} \times 10^{13}$	Constituent B $D_{20} \times 10^7$	Approx. proportion of A and B	Constituents of still finer dispersion
Cotton linters a-cellulose	99.6	0.17	2.12	4.18	2.68	..	..	....	Very sl.
				4.29	2.79	..	..	....	
Absorbent cotton	99.2	..	2.09	4.28	2.64	..	..	....	Somewhat more
Cotton linters filter paper	97.2	..	1.83	3.94	2.83	small amount		. .	Still more
Cross and Bevan aspen wood cellulose	71.2	..	1.98	4.28	2.70	2.73	3.53	2A:1B	Considerable of about 1/8 normal mol. wt. and finer
Cross and Bevan white spruce cellulose	..	..	..	4.05	2.80	2.79	3.87	2B:1A	Same
Sulfite pulp a-cellulose	96.1	0.98	1.97	4.10	2.84	2.74	3.38	2A:1B	Same
Bleached sulfite pulp	81.4	..	1.80	4.28	2.72	2.73	3.67	3B:1A	Same

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[3] Stamm, THIS JOURNAL, 52, 3047 (1930).

at a concentration of 0.10% on the three different cotton celluloses. The results show that practically the same conditions of dispersion must exist for each of the three celluloses. The Z displacement curves for the absorbent cotton are almost identical with those for the cotton linters α-cellulose given in Fig. 2 of the previous paper, except that the deviation from symmetry at the extreme left is somewhat greater. This indicates the presence of a little more material of a much finer state of dispersion. The curves for the cotton linters filter paper show the presence of still more of this material of relatively fine dispersion, together with a small amount of materials of perhaps only half of the molecular weight of the major part. Though the amount of this latter material present is not enough to cause a definite break in the curves, as will be shown to be the case with the wood celluloses, still it is present in sufficient quantities to give a slight decrease in the average sedimentation velocity and a corresponding increase in the calculated diffusion constant. This increase in the calculated diffusion constant is caused by a slight spreading of the sedimentation boundaries of the two constituents.[4] The results indicate that the three cotton celluloses are practically monodisperse with only relatively small amounts of material of finer dispersion present. The amount of this material of relatively fine dispersion present seems to decrease with an increase in the a-cellulose content.

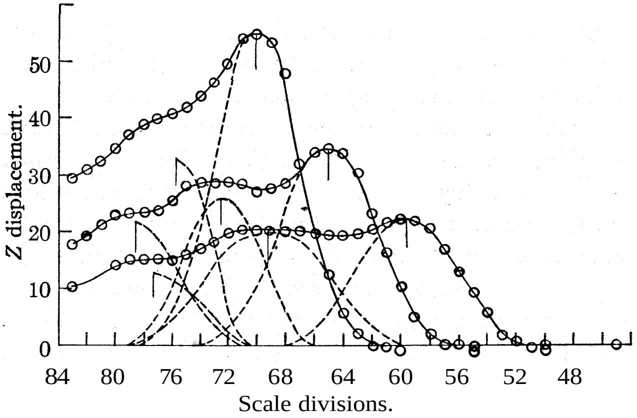

Fig. 1.—Photographic scale displacements for a run on Cross and Bevan aspen cellulose.

Wood Cellulose.—Figure 1 gives the results for the Cross and Bevan aspen cellulose. The curves are quite different from those for cotton cellulose (Fig. 2 of previous paper). Instead of being symmetrical with but one maximum, the curves are decidedly unsymmetrical and show at least three maxima. The right-hand maxima correspond very closely to the positions

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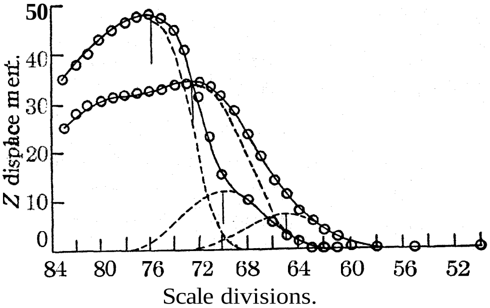
[4] Svedberg and Stamm, THIS JOURNAL, 51, 2170 (1929).

of the sedimenting boundaries of the molecular species found to be present in the cotton celluloses, as is shown by the sedimentation velocity values calculated from these maxima (see constituent A, Table II). Further, if the diffusion is calculated from the sections of the curves to the right of these maxima, values comparable with the diffusion values for cotton cellulose are obtained (see constituent A, Table II). If then the curves representing the molecular species present in cotton cellulose are completed by making the left-hand section symmetrical with the right-hand section (represented in the figure by the dotted lines), it is then possible to obtain the curve which, combined with the one just constructed, will give the experimental curve. In this way the curve for the second constituent (B in Tables I and II) is constructed. The sedimentation velocity calculated for constituent B is practically equal to the two-thirds power of the sedimentation velocity of constituent A, which indicates that it has a molecular weight of just half that of constituent A.

$$M_A = M_B (s_A/s_B)^{3/2}$$

This is further confirmed from the values of the diffusion constant calculated from the corresponding curves, as

$$s_A/D_A = 2s_A/D_B$$



Fig, 2.—Photographic scale displacements for a run on bleached sulfite pulp.

It is difficult to apply this analysis further to get the molecular weight of the materials of still finer dispersion. There are indications of a material of one-eighth of the normal molecular weight being present, together with still finer dispersed material. A material of one-fourth of the normal molecular weight may also be present. The overlapping of the individual curves, which become closer and closer together as the size of the particles decreases, makes it impossible to determine just what constituent curves really make up the experimental composite curve in this zone.

Figure 2 gives the results for the bleached sulfite pulp. An analysis of the data indicates that both constituents A and B are present, together with still more finely dispersed material. The proportions of constituent A and constituent B are, however, quite different from the proportions present in the aspen Cross and Bevan cellulose. Unfortunately, the base line of the curves cannot be determined with sufficient accuracy so as to obtain the exact proportions of the various constituents from the relative areas under each of the curves. The approximate proportions are given, however, in Table I.

TABLE II

RESULTS OF A SEDIMENTATION VELOCITY RUN MADE WON A 0.10% SOLUTION OF ASPEN CELLULOSE PREPARED BY THE CROSS AND BEVAN METHOD

Copper concn. of solvent, 1.28%; NH_3 concn. of solvent, 22.0%; V = 0.642; ρ = 0.9474; rel. visc. of solvent, 1.390; age of solution at time of starting run, 0.5 hr.; length of column of solution, 1.26 cm.; thickness of column, 1.20 cm.; average speed, 42,900 r. p. m.; time interval between exposures, 40 min.; av. temp., 20.7°.

Sedimentation. Constituent **A**

Ax in scale div.	$\frac{\Delta Z \text{ max.}}{2G}$ cm.	Ax corr., cm.	x mean, cm.	ω^2 $\times 10^{-7}$	s_{20} cm./sec. per cm./sec.^{2} $\times 10^{13}$
4.8	0.0076	0.1006	4.81	2.02	4.25
5.0	.0042	.1005	4.91	2.02	4.16
5.5	.0026	.1085	5.02	2.00	4.43
				Av.	4.28

Constituent B

Ax in scale div.	$\frac{\Delta Z \text{ max.}}{2G}$ cm.	Ax corr., cm.	x mean, cm.	ω^2 $\times 10^{-7}$	s_{20} cm./sec. per cm./sec.^{2} $\times 10^{13}$
3.2	0.0024	0.0641	4.82	2.20	2.70
3.3	.0019	.0655	4.88	2.00	2.75
				Av.	2.73

Diffusion. Constituent **A**

Time, sec.	$2\,\Delta x_2$ in scale div.	$(\Delta x_2 \text{ corr.})^2$	h	α	D_{20} cm.^{2}/sec. $\times 10^7$
5,160	6.8	0.00430	10.7	5.2	2.83
7,560	8.0	.00594	13.3	6.2	2.52
9,960	8.0	.00594	7.1	4.1	2.66
12,360	7.7	.00550	4.0	2.7	2.78
				Av.	2.70

Constituent B

Time, sec.	$2\,\Delta x_2$ in scale div.	$(\Delta x_2 \text{ corr.})^2$	h	α	D_{20} cm.^{2}/sec. $\times 10^7$
7,560	6.0	0.00335	3.6	2.6	3.33
7,560	4.4	.00180	2.1	1.8	3.73
9,960	6.8	.00430	2.7	1.9	3.02
9,960	5.0	.00233	1.7	1.45	3.60
12,360	8.2	.00625	1.5	1.1	3.96
				Av.	3.53

Time permitted making comparative measurements on the different celluloses only at one cellulose concentration, namely, 0.10%. It seems highly probable, however, that the increase of the diffusion constant with decreasing concentration of cellulose will be similar to that reported in the previous paper for the cotton linters a-cellulose even in the case of the wood celluloses. No great error can be introduced by making this assumption, as calculations made from the specific sedimentation velocity alone, using Stokes' law, give the same order of molecular weight. As the molecular weight of constituent A from the previous paper is 40,000 ± 5000 on a copper-free basis, then the molecular weight of constituent B should be 20,000 and the number of simple glucose units in a particle should be 100 to 130.

The present data indicate that the difference between isolated wood cellulose and cotton cellulose is largely a difference in the degree of association of the structural building units and perhaps also in the manner in which the fundamental building units are put together. Unfortunately, the author did not have time to carry this work further so as to determine whether these differences between cotton and isolated wood celluloses are inherent differences in the celluloses as they exist in nature, or if the chemical treatment used in isolation has caused a partial dissociation of the wood cellulose. This question and many others of interest might be answered by a continuation of this work. The author hopes to be able to build a centrifuge to continue the work in the United States, but at present he is uncertain whether this will be possible.

The author again wishes to express his sincere thanks to Professor The Svedberg for the use of the ultracentrifuge equipment of this Laboratory, and for the help which he always freely gave toward the carrying out of this research.

Summary

1. The nature of the dispersion in cuprammonium solvent of several different isolated wood celluloses was compared with that of cotton cellulose with the aid of the ultracentrifuge.

2. The cotton celluloses are monodisperse with but a very small amount of a considerably finer material present.

3. The amount of this more finely dispersed material present seems to decrease with an increase in the a-cellulose content.

4. The isolated wood celluloses show the presence of a material of the same molecular dispersion as that of cotton cellulose together with a material of one-half of this molecular weight, and molecular species of still finer dispersion.

5. The data thus indicate that the difference between isolated wood cellulose and cotton cellulose dissolved in cuprammonium solvent is at least partially a matter of difference in the degree of association of similar structural building units.

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SEPARATION AND IDENTIFICATION OF THE ALKALI AND ALKALINE EARTH METALS USING ISOAMYL ALCOHOL

BY HERMAN YAGODA

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Introduction

The method employed for separating and identifying sodium, potassium, magnesium, calcium, barium and strontium in the usual scheme of qualitative analysis for those ions is to precipitate the calcium, barium and strontium as carbonates from ammoniacal solution using a highly concentrated solution of ammonium carbonate as reagent, and leave sodium, potassium and magnesium in solution,[1] or to use ethyl alcohol along with the ammonium carbonate and thereby cause magnesium to precipitate along with the alkaline earth carbonates[2] These separations, in general, are satisfactory, but require considerable time to execute.

The basis of the method of analysis here proposed is that the bromides of sodium, potassium and barium are insoluble in isoamyl alcohol (commonly called amylic or simply amyl alcohol) and that calcium, strontium and magnesium bromides are soluble in that alcohol. An advantage of this separation, from the qualitative point of view, is that traces of sodium, such as are usually introduced during the course of analysis from the glassware and reagents remain in solution along with the soluble bromides; therefore, if further analysis of the insoluble portion reveals the presence of sodium, it may be assumed with assurance that the sodium so found is not foreign to the sample being analyzed. Also, as barium is a metal of relatively rare occurrence, the presence of a portion of salt insoluble in the isoamyl alcohol may usually be taken as an indication of the presence of alkali salts in the sample.

Apparatus

The apparatus required for this separation of the metals into two groups and for the subsequent analysis of each group consists of: (1) a 30-cc. pyrex glass beaker and an iron or nickel crucible 1.5" in diameter. The metal crucible both serves as an air-bath for the beaker, preventing spattering of the liquid being heated, and also keeps the bottom of the beaker free from films of dirt which make difficult the detection of small residues left by the evaporation of liquids (see Fig. 1); (2) the filtering apparatus—

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[1] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., 1929, Vol. I, 5th ed., pp. 118–120.

[2] Bray, THIS JOURNAL, 31, 611 (1909); Noyes, "Qualitative Chemical Analysis"; Noyes and Bray, "A System of Qualitative Chemical Analysis for the Rare Elements," p. 236.

a side-necked test-tube, or small suction flask, in which a small test-tube is placed to catch the filtrate and (3) a 1-cc. and a 3-cc. pipet.

The use of this small apparatus keeps the substance being analyzed in a concentrated form with the result that small samples may be taken for investigation and the time of analysis greatly shortened thereby.

Procedure for the Separation and Identification of the Alkali **and** Alkaline **Earth** Metals.—The solution, which has been freed from members of the first, second and third groups in accordance with the customary procedure, is boiled until all hydrogen sulfide gas is expelled, and (then until) its volume is about 5 cc. (a). At this point the liquid is filtered into the small 30-cc. beaker, 1 cc. of 16 *N* nitric acid is added, and the solution is evaporated to dryness. The heating is then continued until all ammonium compounds are volatilized (b).

The residue in the beaker is treated with 1 cc. of concentrated hydrobromic acid (48.5% HBr, approximately 8 N) and evaporated to dryness, avoiding strong overheating (c). When cool, the residue is pulverized with the stirring rod, 3 cc. of isoamyl alcohol is added, the mixture is heated to ebullition and maintained at boiling for about half a minute. The mixture is cooled to room temperature and filtered. The *Filtrate* contains magnesium, strontium and calcium bromides; the *Residue* consists of sodium, potassium and barium bromides.

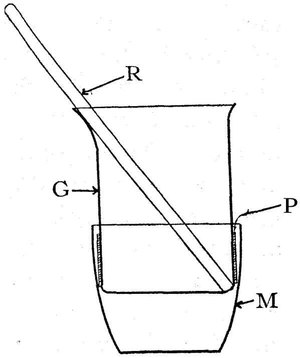

Fig. 1.—Apparatus for digestion and evaporation processes. G, 30-cc. glass beaker; R, glass rod; P, asbestos paper; M, metal crucible.

The ***Residue*** is washed with a few drops of isoamyl alcohol and then subjected to a preliminary flame test examination (d). The appearance of the characteristically colored flame given by any one of the metals may be taken as a test for the presence of that element and its relative quantity may be judged from the size of the residue left by the isoamyl alcohol. Where the residue consists of a mixture of the two alkali metals and barium, a simple qualitative separation may be made as follows. The residue is dried, the bromides removed from the filter paper into a small test-tube, 1–2 cc. of 95% ethyl alcohol and two drops of concentrated hydrobromic acid are added to the tube, the mixture brought to a boil, cooled and then filtered (e). The residue consists chiefly of potassium bromide, which may be dissolved in 1 cc. of water and the solution further tested for potassium with the aid of sodium cobaltinitrite reagent. The alcoholic filtrate contains sodium and barium bromides. Add 0.5–1 cc. of 12 N hydrochloric acid to the solution; a crystalline precipitate of sodium and barium chlorides forms immediately in the presence of appreciable quantities of either of the salts. Cool under running tap water, filter off the crystalline precipitate, saving the filtrate (f), and test the salts in the Bunsen flame. If the color of the flame indicates the presence of barium, as well as that of sodium, the presence of the barium may be further confirmed by dissolving the chlorides in 2 cc. of water and adding a few drops of dilute sulfuric acid; in the presence of barium, a white precipitate of barium sulfate will form.

The Filtrate of magnesium, strontium and calcium bromides dissolved in the isoamyl alcohol is evaporated to dryness, 0.5 cc. of 16 N nitric acid is added and the solution is again evaporated to dryness (g). The dry salts are heated strongly (h) until reddish brown fumes of nitrogen peroxide are no longer evolved (i), then cooled, pulverized with the stirring rod, leached with **3** cc. of water, boiled and filtered. The residue is a mixture of oxide and hydroxide of magnesium, which may be confirmed further by dissolving it in a few drops of hydrochloric acid (j) and then testing the solution with ammonium phosphate in the usual manner (k).[3] The aqueous filtrate is evaporated to dryness, a residue indicating the presence of either strontium or calcium. Cool, and when cold add 1 cc. of 16 N nitric acid, stir for a few minutes and then filter through a paper previously moistened with nitric acid. The crystalline residue is strontium nitrate; this is washed with 0.5 cc. of 16 N nitric acid and further confirmed by any of the usual methods.[4] Hillebrand and Lundell suggest this method for the quantitative separation of strontium from calcium.[5] The presence of calcium in the filtrate may be determined by making the solution ammoniacal, and adding several drops of a saturated solution of ammonium oxalate to the hot alkaline liquor; a white precipitate of calcium oxalate indicates the presence of calcium.

Notes on the Procedure

(a) The only acid radicals present in the solution should be either nitrates or chlorides. Sulfates, if present, are easily removed by treatment with lead nitrate solution, filtering off the lead sulfate and removing the excess lead ion with hydrogen sulfide. **As** nitrates are converted more readily to bromides than chlorides, it is best first to evaporate the residue with **1** cc. of **16** N nitric acid, when preliminary tests indicate the presence of considerable sodium chloride.

(b) Only a small quantity of ammonium salts will be present at this stage of the analysis as most of them are usually introduced in the precipitation of the fourth group by a concentrated solution of ammonium carbonate. Absence of any appreciable white residue may be taken as proof of the absence of Na^+, K^+, Ba^{++}, Mg^{++}, Sr^{++} and Ca^{++}.

(c) Overheating will decompose magnesium bromide. If this has occurred, the insoluble magnesium compound may be brought back to solution by adding a drop of concentrated hydrobromic acid to the isoamyl alcohol used in the separation.

(d) The bromides of sodium, potassium and barium yield the characteristically colored flames more readily than the chlorides.

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[3] Cf. Carl Otto, THIS JOURNAL, 48, 3016 **(1926).**

[4] **S. G. Rawson, J.** *Soc. Chem. Ind.*, **16, 113 (1897).**

[5] "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, p. **491.**

(e) If the residue left by the isoamyl alcohol is small, only 1 cc. of ethyl alcohol should be used in making the separation. Very small residues are best handled at this point by placing the small filter paper in the tube and digesting it with the alcohol along with the bromide salts. By properly folding the paper the potassium may be kept on it, and then removed for further examination by leaching the paper with water.

(f) Where the presence of potassium in quantities less than 1 mg. is sought and more than *2* cc. of ethyl alcohol was used in the separation, this filtrate should be evaporated to dryness and the residue subjected to a flame test.

(g) The nitric acid removes traces of organic matter left by the decomposition of the isoamyl alcohol. Negligibly small residues will usually appear at this point even in the absence of Mg^{++}, Ca^{++} and Sr^{++} owing to the solution by the isoamyl alcohol of Na^+, K^+ and Ba^{++} to the extent of less than one milligram of total metal.

(h) A gas flame about one inch high and whose tip just covers the base of the crucible will be found convenient for most of the heating processes in this procedure. For the decomposition of the magnesium nitrate, however, the flame should be about three inches high and of sufficient intensity to maintain the portion of the crucible below the beaker at a red heat. The decomposition process may be followed by noting the evolution of nitrogen dioxide vapors, whose color is made very pronounced by the white background of magnesia.

(i) Magnesium nitrate decomposes at a temperature much below the melting point of either strontium or calcium nitrate, neither of the latter showing any tendency to decompose at their respective melting points.

(j) Where such magnesium is present, the magnesium oxide cakes and a portion of it adheres to the scratches in the bottom of the beaker. In such cases, after the leaching and filtration, the hydrochloric acid should be added first to the beaker so as to dissolve the remaining magnesia, and then that liquor is poured through the magnesia on the filter paper.

(k) Owing to the absence of ammonium salts the magnesium ammonium phosphate precipitates without any difficulty.

(l) Strontium nitrate not being very volatile does not give a good flame test. The residue should therefore be moistened with hydrochloric or hydrobromic acid before applying the flame test. The formation of a persistent turbid liquid is in itself a delicate test for strontium, as the nitrate residue dissolves very readily in cold nitric acid when only calcium is present, forming a clear solution.

Experimental Basis of the Procedure

All the salts used in this study were prepared and purified by well-known methods. The isoamyl alcohol employed for the solubility measurements boiled between 129–130°; a C. P. product was used without further purification in studying the separations qualitatively. The 95% ethyl alcohol used in this work had a specific gravity of **0.7999.**

The solubility data assembled in Tables I to V were obtained by evaporating approximately 5-cc. portions of saturated solution of known weight in small quartz dishes and determining the weight of the solid residue left in the dish by difference. The solvent was prepared by diluting approximate quantities of concentrated hydrobromic acid with the alcohol in question and then measuring its acidity by titration with standard alkali. The solutions were prepared by digesting portions of the solvent with an excess of solute, raising the mixture to a boil, immediately cooling for a moment under tap water and then allowing the system to reach equilibrium at a slower rate in a thermostat at 25°. This method of preparing the solution, though giving a slightly supersaturated one, was thought advisable in so far as it duplicated conditions as directed in the procedure.

TABLE I

SOLUBILITY OF THE DIFFERENT BROMIDES IN ISOAMYL ALCOHOL AT 25° (SP. GR. OF SOLVENT, 0.805)

Salt	G. of salt per cc. of solvent	Mg. of metal per 3 cc. of solvent
NaBr	0.00085	0.67
KBr	.000014	.014
$BaBr_2$	.00013	.017
$SrBr_2$	.305	324.0
$MgBr_2$	Very soluble	
$CaBr_2$	Very soluble	

The solubility data show that a satisfactory separation of the above salts into two groups can be effected by isoamyl alcohol.

TABLE II

SOLUBILITY OF SODIUM BROMIDE IN ISOAMYL ALCOHOL CONTAINING HYDROBROMIC ACID, AT 25°

Normality of solvent	Sp. gr. of solvent	G. of NaBr per cc. of solvent	Mg. of metal per 3 cc.
0	0.805	0.00085	0.67
0.066	.8166	.00124	0.84
.181	.8262	.00174	1.17
.463	.850	.00274	1.83
.764	.8754	.0039	2.61

The data in Table II show that the solubility of sodium bromide in isoamyl alcohol cannot be diminished by the addition of hydrobromic acid to the solvent.

The solubility data in Tables III and IV show that the addition of hydrobromic acid to ethyl alcohol causes the solubility of sodium bromide to increase steadily, whereas, in the case of potassium bromide, the solubility first diminishes, and then upon further addition of acid increases. The

TABLE III

SOLUBILITY OF SODIUM BROMIDE IN 95% ETHYL ALCOHOL AT 25°

Normality	Sp. gr.	G. of NaBr per g. of solvent	Mg of Na per cc. of solvent
0	0.7997	0.0397	7.1
0.100	.810	.0404	7.4
.162	.815	.0425	7.8⁻
.204	.820	.0425	7.8
.337	.833	.0448	8.3
.629	.862	.0457	8.8
.800	.878	.0435	8 5⁺
.954	.893	.0455	9.1

TABLE IV

SOLUBILITY OF POTASSIUM BROMIDE IN 95% ETHYL ALCOHOL AT 25°

Normality	Sp. gr.	G. of KBr per g. of solvent	Mg. of K per cc. of solvent
0	0.7997	0.00289	0.76^-
0.050	.805	.00191	$.50^+$
.100	.810	.00165	.44
.204	.820	.00162	$.43^+$
.400	.839	.00176	$.48^+$
.537	.853	.00186	.52
.800	.878	.00190	.60
.954	.893	.00242	.71

solubility of potassium bromide is a minimum when the acidity of the alcohol is 0.2 *N* in hydrobromic acid; under these conditions the solvent will dissolve 43 mg. of sodium bromide and 1.6 mg. of potassium bromide per cc.

TABLE V

SOLUBILITY OF SALTS IN 95% ETHYL ALCOHOL 0.2 *N* IN HYDROBROMIC ACID AT 25°

Salt	G. of salt per cc. of solvent	Mg. of metal per cc. of solvent
KBr	0.0016	0.44
NaBr	.043	7.8
$BaBr_2$	.022	10.0
KCl	.0042	2.2
NaCl[a]	.00094	0.37
$BaCl_2$[a]	.00026	.17

[a] Figures refer to the solubility in a solution obtained by adding 1 cc. of 11.2 *N* hydrochloric acid to 2 cc. of saturated solution of sodium bromide or barium bromide in the above ethyl alcohol.

The data of Table V show that a qualitative separation of potassium from sodium and barium may be effected by solution of the last two in ethyl alcohol 0.2 *N* in hydrobromic acid; that sodium chloride and barium chloride precipitate almost quantitatively upon addition of concentrated hydrochloric acid to the alcoholic solution of the bromides; also, that the solvent can dissolve more potassium chloride than is formed by the reaction of the hydrochloric acid upon the small quantity of potassium bromide that enters into solution along with the sodium and barium bromides.

Qualitative Study of Procedure

Solutions of the chlorides of sodium, potassium, barium, magnesium, strontium and calcium were prepared of such strength that 1 cc. of the solution contained 10 mg. of the metal. Definite volumes of these solutions were mixed together and then analyzed in accordance with the proposed procedure. The samples so analyzed are tabulated in Table VI, the numbers representing the milligrams of the metal present in the sample.

Conversion of Salts to Bromides with Concentrated Hydrobromic Acid.—The utility of the procedure depends upon the ease with which the

TABLE VI

ANALYTICAL DATA

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Na^+	10	..	..	..	..	20	..	..	..	..	..	50	..	..	..	..	50	5	..	2
K^+	5	..	20	..	10	..	20	..	..	..	..	..	25	..	..	..	..	10	2	5
Ba^{++}	10	..	..	10	..	..	..	20	..	..	..	..	..	50	..	..	..	5	..	2
Mg^{++}	10	..	..	10	..	..	..	..	..	50	..	..	..	..	25	25	..	5	20	2
Ca^{++}	10	..	5	..	20	..	..	..	..	..	50	..	25	..	25	..	50	20	5	30
Sr^{++}	5	50	10	..	..	..	..	..	20	..	..	..	..	..	..	25	..	5	10	5

acid radicals, commonly associated with the metals, can be converted to bromides with concd. hydrobromic acid. Definite weights of different salts were taken such that 50 mg. of metal was present in each case and evaporated to dryness with 1 cc. of hydrobromic acid in the apparatus of Fig. 1. The residue was then tested qualitatively for the replaced acid constituent. The results are shown in Table VII.

TABLE VII

EXPERIMENTAL RESULTS

Salt	Number of treatments	Quantity of replaced radical	Salt	Number of treatments	Quantity of replaced radical
$SrCl_2 \cdot 4H_2O$	1	None	$NaNO_3$	1	Trace
KCl	1	Trace	$BaCl_2 \cdot 2H_2O$	1	Trace
NaCl	1	Fairly large	$CaCl_2 \cdot 6H_2O$	1	Trace
NaCl	2	Small	$MgCl_2 \cdot 6H_2O$	1	None

The presence of sulfates interferes with this separation of the alkali and alkaline earth metals. If present, the sulfates are best removed by treating the filtrate from the third analytical group with a lead nitrate solution, filtering off the lead sulfate and then removing the excess lead ion by saturating the solution with hydrogen sulfide gas.[6] The alkaline earth sulfates, being insoluble in water, will precipitate at an early stage of the analysis of the sample. These sulfates are first converted to carbonates by boiling with a concentrated sodium carbonate solution;[7] the carbonates are then dissolved in dilute hydrobromic acid and the solution is joined with the alkali bromides.

The treatment of the bromides of barium, potassium and sodium with ethyl alcohol is not made with the view of quantitatively separating the sodium and barium from potassium, but to get a solution (most frequently containing sodium only) from which sodium and barium can be precipitated with as simple a reagent as concentrated hydrochloric acid.

Summary

A method for separating and identifying a mixture containing sodium, potassium, barium, magnesium, strontium and calcium has been proposed whose essential features are as follows.

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[6] Noyes and Bray, "Qualitative Analysis for the Rare Elements," p. 254.

[7] Noyes and Bray, *ibid.*, p. 51.

SCHEME OF ANALYSIS OF THE ALKALI AND ALKALINE EARTH METALS

<table>
<tr><td colspan="7">Solution of nitrates or chlorides of Na, K, Ba, Mg, Sr and Ca; evaporate to dryness, add 1 cc. of 8 N HBr, toil off acid, cool, pulverize residue, digest with 3 cc. of isoamyl alcohol and filter.</td></tr>
<tr><td colspan="4">Residue.—NaBr, KBr and $BaBr_2$: Make flame test. Boil residue with 1–2 cc. of ethyl alcohol, add 1–2 drops of 8 N HBr, cool and filter.</td><td colspan="3">Filtrate.—$MgBr_2$, $CaBr_2$ and $SrBr_2$. Boil off the isoamyl alcohol, add 0.5 cc. of 16 N HNO_3 and evaporate to dryness. Residue: $Mg(NO_3)_2$, $Ca(NO_3)_2$ and $Sr(NO_3)_2$. Heat strongly, cool, add 3 cc. of water, boil and filter.</td></tr>
<tr><td rowspan="3">Precipitate.—Chiefly KBr. Dissolve in 1 cc. of water and add 2 cc. of $Na_3Co(NO_2)_6$ reagent. A yellow ppt. confirms the presence of potassium.</td><td colspan="3">Solution.—Contains NaBr and $BaBr_2$. Add 0.5–1 cc. of 12 N HCl, cool and filter.</td><td rowspan="3">Residue.—MgO and $Mg(OH)_2$. Redissolve in 1 cc. of 6 N HCI, add 1 cc. of 1 N $(NH_4)_2HPO_4$ soln. and 2 cc. of 16 N NH_4OH. A white precipitate of ($MgNH_4PO_4$) confirms the presence of magnesium.</td><td colspan="2">Filtrate.—Contains $Ca(NO_3)_2$ and $Sr(NO_3)_2$. Evaporate to dryness, cool, add 1 cc. of 16 N HNO_3, stir and filter, moistening paper with nitric acid.</td></tr>
<tr><td colspan="2">Precipitate.—Mixture of NaCl and $BaCl_2$. Make flame test. Dissolve salts in 1 cc. of water, add a few drops of 6 N H_2SO_4. Roil and filter.</td><td rowspan="2">Filtrate.—May contain trace of potassium.</td><td rowspan="2">Precipitate.—$Sr(NO_3)_2$: Moisten with 12 N HCl and test in flame.</td><td rowspan="2">Filtrate.—$Ca(NO_3)_2$: Make alkaline with 16 <i>N</i> NH_4OH, add 1 cc. of saturated $(NH_4)_2C_2O_4$ soln. White precipitate confirms calcium.</td></tr>
<tr><td>Precipitate.—$BaSO_4$: Confirms presence of barium.</td><td>Filtrate.—Na_2SO_4: Evaporate, moisten residue with 12 N HCl and test in gas flame.</td></tr>
</table>

1. The conversion of the chlorides or nitrates to bromides with 8 *N* hydrobromic acid.
2. Separation of sodium, potassium and barium bromides from magnesium, strontium and calcium bromides using isoamyl alcohol.
3. Separation of sodium and barium bromides from potassium bromide using ethyl alcohol.
4. Precipitation of sodium and barium chlorides with 12 N hydrochloric acid from the ethyl alcohol solution.
5. Separation of magnesium from calcium and strontium by ignition of the nitrates.
6. Separation of strontium from calcium by dissolving calcium nitrate in 16 N nitric acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

STUDIES ON THE PERIODIC SYSTEM. III. THE RELATION BETWEEN IONIZING POTENTIALS AND IONIC POTENTIALS

BY G. H. CARTLEDGE

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In the preceding papers of this series[1] the author has developed a quantitative periodic function, the ionic potential ϕ, which is defined as the ratio of the charge of an atomic ion to its crystal radius, that is

$$\phi = \frac{z}{r} \qquad (1)$$

In the previous papers the numerical values of the ionic potentials were calculated in arbitrary units, taking z as the valence and r as the ionic radius in Ångström units. It has been shown that the values of the ionic potential may be used to trace the order of variation in numerous properties of ions and compounds, such as the development of acidic properties of hydroxides, the electrical conductance and volatility of chlorides, and others. It is the purpose of the present paper to show the relationship between the ionic potential and the ionizing potential; from this relationship it is found that information regarding the polarizability of the ions may be obtained.

In order to make the desired comparisons it will be convenient to express the ionic potential in volts. The potential of a positive ion of valence z and charge ze e. s. u. is ze/r_c in electrostatic units, if r_c is the ionic radius in cm. As the volt is one three-hundredth of the electrostatic unit of potential, we have for ϕ_v, the ionic potential in volts

$$\phi_v = 300 \frac{ze}{r_c} \text{ volts} \qquad (2)$$

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[1] Cartledge, THIS JOURNAL, 50, 2855, 2863 (1928).

but ϕ was previously defined arbitrarily as the ratio of the valence to the radius in Ångström units, so we have

$$\phi_v = \frac{300 \times 4.774 \times 10^{-10}}{10^{-8}} \phi = 14.3\phi \qquad (3)$$

In Table I the values of ϕ_v as well as the ionization potentials[2] are given for reference. In the case of the ionization potentials the data refer to the removal of the *last* electron in producing the ion represented by the symbol. The ionizing potential is denoted by V.

TABLE I

IONIC AND IONIZING POTENTIALS (VOLTS)

	H^+					
ϕ_v	...					
V	13.54					
	Li^+	Be^{++}	B^{3+}	C^{4+}	N^{5+}	
ϕ_v	23.9	92.3	215	380	645	
V	5.37	18.1	37.8	64.2	...	
	Na^+	Mg^{++}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}
ϕ_v	15.0	44.4	85.9	140	210	296
V	5.12	14.97	28.32	44.95	64	...
	K^+	Ca^{++}				
ϕ_v	10.4	28.9				
V	4.32	11.82				
	Rb^+	Sr^{++}				
ϕ_v	9.65	25.3				
V	4.16	10.98				
	Cs^+	Ba^{++}				
ϕ_v	8.45	21.2				
V	3.88	9.96				
	87^+	Ra^{++}				
ϕ_v		...				
V	...	10.23				

The Theoretical Relation between Ionic and Ionizing Potentials.—The theoretical relationship between the ionic and ionizing potentials may be qualitatively derived by using the Bohr model of the atom, augmented by considerations growing out of the more recent picture given by the wave mechanics. According to the considerations of Bohr, the valence electron rotating in its orbit has both kinetic and potential energy. If r is the radius of the orbit, the kinetic energy is $e^2/2r$ and the potential energy is $-e^2/r$. The total work done in bringing up the electron from an infinite distance is the sum of these energies, $-e^2/2r$, and is measured by the ionization potential. In comparing the ionic potential with the ionizing potential, the potential energy of the electron is the important quantity,

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[2] Foote and Mohler, *Bull. Nat. Res. Council*, **9**, No. 48 (1924).

and this is numerically twice the ionization work. The ionic potential, therefore, will be compared with double the ionization potential.

It is not possible to make a theoretical estimate of the relation between these quantities, however, since the Bohr model gives no information as to the relation of the crystal radius of the ion to the electronic orbit of the neutral atom. A closer approach to this information may be obtained from the wave mechanics conception of the atom.[3]

In Fig. 1, the solid curves of which are taken from Pauling's paper, the electron distribution in the sodium and chloride ions is given as a function of the distance from the nucleus. The distance to which these ions approach each other in the sodium chloride crystal is such that a slight penetration of their electronic fields takes place; that is, the crystal radius r_c corresponds to the distance at which the electron distribution becomes approximately equal to zero, as indicated in the figure. If we assume for the moment that the valence electron of the sodium atom may be added without disturbing the spherical distribution of the K and L electrons in the ion, according to the dotted, qualitative extension of Pauling's curve, r_e in the figure will represent the electron radius which determines the ionization work. With the situation as represented in the diagram, the doubled ionizing potential should be less than the ionic potential by an amount equivalent to the work done in moving the static electron from r_c to r_e.

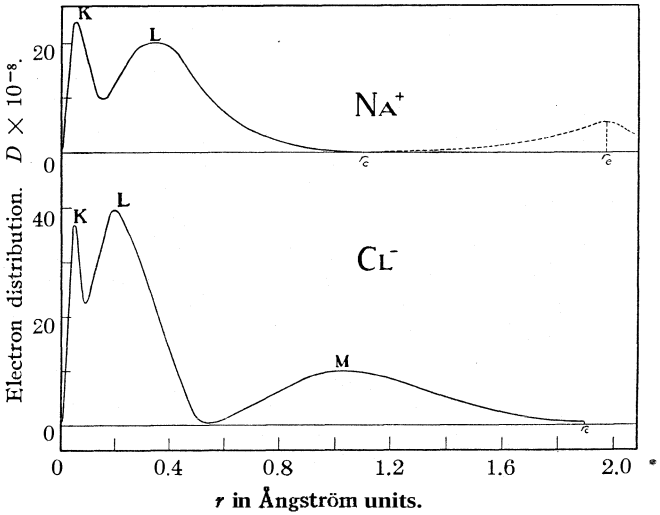

Fig. 1.

That this difference should be definitely related to the ionic potential may be indicated as follows. The work done, *w*, is given by

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[3] Pauling, This Journal, 49, 765 (1927).

$$w = -\int_{r_c}^{r_e} \frac{ze^2dr}{r^2} = ze^2\left(\frac{1}{r_c} - \frac{1}{r_e}\right) \text{ ergs} \tag{4}$$

$$w = \frac{ze^2}{10^7\, r_c}\left(1 - \frac{r_c}{r_e}\right) \text{ joules} \tag{5}$$

but ϕ_v is the potential at r_c and $2V$ is the potential at r_e, so if Δ_v is the difference $\phi_v - 2V$ we have, with e still in e. s. u.

$$w = \frac{\Delta_v e}{3 \times 10^9} = \frac{ze^2}{10^7\, r_c}\left(1 - \frac{r_c}{r_e}\right) \text{ joules} \tag{6}$$

or, from (2)

$$\|$$

$$\Delta_v = , \left(1 - \frac{r_c}{r_e}\right) \text{ volts} \tag{7}$$

Although it is not possible to predict from either atomic model just what value the fraction r_c/r_e will have in general, further consideration of Fig. 1 will furnish an estimate for the limiting case of a rigid ion of lithium-like structure. The minimum in the electron-distribution curve between the peaks associated with the K and L shells corresponds to the crystal radius r_c in an ion having only the K shell, whereas the L peak corresponds to the radius r_e of the valence electron. The difference between these distances divided by the distance of the L maximum should therefore be approximately equal to the factor $1 - (r_c/r_e)$ in Equation 7. When these distances are measured as closely as the original figure permits, both the Na^+ and Cl^- curves give a value of 0.52. In the sodium and chloride ions the K and L shells are quite rigid, and for such a case Equation 7 accordingly becomes

$$A, = 0.52\phi_v \tag{8}$$

Of the univalent positive ions, the lithium ion is assuredly the most rigid, and it is observed that the equation above corresponds closely to the facts:

$$\phi_v = 23.9 \qquad 2V = 10.74 \qquad \text{A,} = 13.2 = 0.55\phi_v$$

That the relationship cannot be of general applicability, however, is indicated by the consideration that the ions are not rigid. The valence electron has about it an electric field of enormous magnitude, and by its proximity to the ion produces a deformation or polarization which is far greater than the effects produced by light waves or by the proximity of oppositely charged ions. The effect of polarization by electrons has been investigated by Schrödinger.[4] The result of such polarization, in the present case, will be to decrease r_e with respect to r_c; that is, the term $1 - (r_c/r_e)$ (which is equal to Δ_v/ϕ_v) will become smaller as the polarizability of the ion increases. That this actually occurs is shown in Table II, which gives the values of Δ_v/ϕ_v.

It is clear that as far as the fifth series the proportionality factor increases in passing from Group I to the higher groups. The increasing charge **and** decreasing size of the ions makes the polarizability of these ions steadily

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[4] **Schrodinger, Ann.** *Physik,* [4] **77,** 43 (1925).

TABLE II

RATIO $\Delta_v:\phi_v$

Group		I	II	III	IV	V
		→ Decreasing polarizability →				
Series II	↑ Decreasing polarizability	Li^+	Be^{++}	B^{3+}	C^{4+}	
		0.55	0.61	0.65	0.66	
III		Na^+	Mg^{++}	Al^{3+}	Si^{4+}	P^{5+}
		0.32	0.33	0.34	0.36	0.39
IV		K^+	Ca^{++}			
		0.173	0.183			
V		Rb^+	Sr^{++}			
		0.138	0.134			
VI		Cs^+	Ba^{++}			
		0.082	0.061			

less. There is no a *priori* basis for estimating the extent of the change in going down a group, but the deformability of the alkali ions, for example, increases rapidly in passing from lithium to cesium,[5] which corresponds to the great decrease in the ratio observed in the table. From the empirical relation between the ionic and the ionizing potentials we may, therefore, reason backward to obtain further information as to the ionic deformabilities.

Empirical Relation of the Potentials.—When, for the ions of a given periodic series, the differences between the ionic potential and the doubled ionizing potential are plotted against the ionic potential, a smooth curve is obtained suggesting a relation of the type

$$\Delta_v = a\phi_v^b \tag{9}$$

Accordingly, if log Δ_v is plotted against log ϕ_v, as in Fig. 2, it is found that the data for the lithium and sodium series give straight lines. The curves are essentially parallel for the periodic Series II, III and IV. The slope becomes about unity for Series V (rubidium and strontium), whereas with cesium and barium the slope is less than unity. Corresponding to the greater polarizability of the ions in going down a group, the curves lie progressively below each other. The curves for the ions of Series II and III are best represented by the equations

$$\text{Series II} \quad \Delta_v = 0.461\phi_v^{1.061}$$
$$\text{Series III} \quad \Delta_v = 0.274\phi_v^{1.055}$$

The data for potassium and calcium undoubtedly establish a similar curve for series IV, which could be extrapolated to estimate the ionizing potential that scandium would have if the third valence electron were in the 4_0 shell, and similarly for the remaining ions in the series.

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[5] Compare the molecular refractions of the ions, for example, Fajans and Joos, *Z. Physik*, 23, 1 (1924).

When we plot Δ_v against ϕ_v for the ions of a particular group, as shown in the upper left portion of Fig. 2, an almost linear curve is obtained. This curve may be extrapolated to $\Delta_v = 0$, at which condition the ionic potential and doubled ionizing potentials are equal; that is, *the valence electron exerts so great a polarizing effect upon the ion that the electron comes as close to the nucleus as the "surface" of a negatively charged ion does.* **At** still

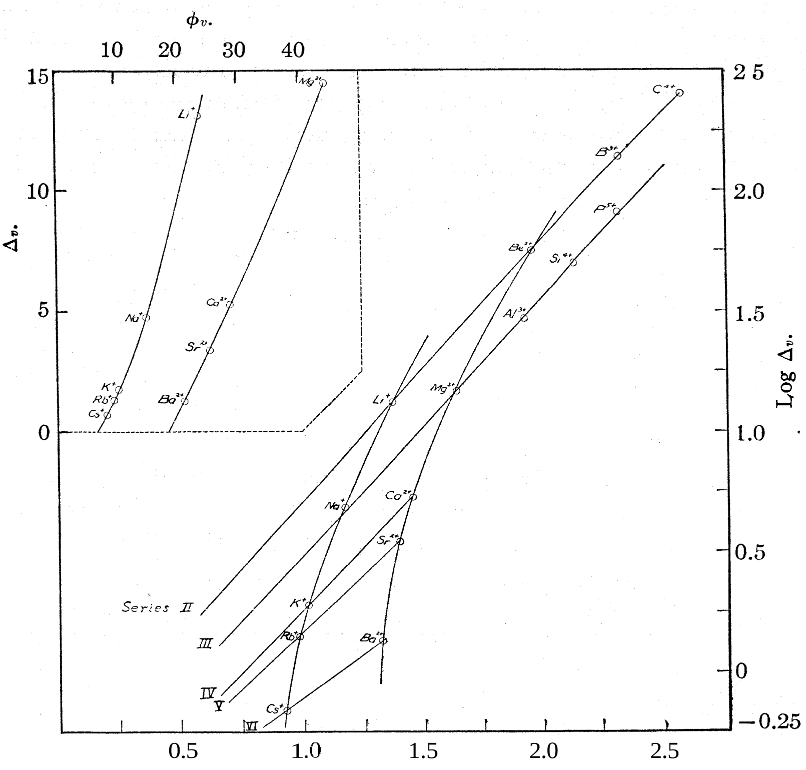

Fig. 2.

smaller values of ϕ_v the electron comes inside the crystal radius. From the values of ϕ_v at which A, = 0, it may be calculated that this occurs, for univalent ions, when the crystal radius is 1.99 Å., and, for bivalent ions, when the crystal radius is 1.54 Å. These radii are only **0.3** Å. and 0.2 Å. larger than the radii of the cesium and barium ions, respectively.

The fact that in barium ions the crystal radius is even closer to the critical size (for $\Delta_v = 0$) than it is in cesium may readily account for the fact that, in Fig. 2, the cesium–barium curve has a slope so much less than the curves above it. In spite of the increase in charge, which generally decreases polarizability, the nearer approach of the barium valence electron to the ion "surface" gives a greater polarization in barium than in cesium (Δ_v/ϕ_v = 0.082 for *Csf* and 0.061 for Ba^{++}).

The Ionic **Polarizability.**—On account of the close relationship obviously existing between the polarizability of the ions and the difference in the potentials under consideration, it will be interesting to compare the ionic polarizabilities as measured by other types of phenomena. Reference has already been made[4] to the work of Schrödinger, in which the polarization of the ion by the valence electron is calculated from spectral data. Another related type of phenomenon is the ionic refraction, data for which are given by Fajans and Joos.[5] The required data are assembled in Table III, in which p represents the index of refraction as calculated by Schrödinger,[6] p' the ionic refraction[5] and Δ_v/ϕ_v has its previous significance.

Table III

Ionic Polarizabilities

	$\frac{\Delta_v}{\phi_v}$	p	p'		$\frac{\Delta_v}{\phi_v}$	p	p'
C^{4+}	0.664	1.4	..	Mg^{++}	0.326	30	..
B^{3+}	.647	2.6	..	Na^+	.32	26(?)	0.50
Be^{++}	.608	4.2	..	K^+	.17	326	2.23
Li^+	.553	15	0.20	Rb^+	.138	711	3.58
Si^{4+}	.358	14	..	Cs^+	.082	1160	6.24
Al^{3+}	.342	19	..				

The data of Schrodinger are plotted against Δ_v/ϕ_v in Fig. 3, from which it is obvious that a smooth curve fits nicely, although the table includes the entire alkali family, together with ions up to Group IV in Series II and III.

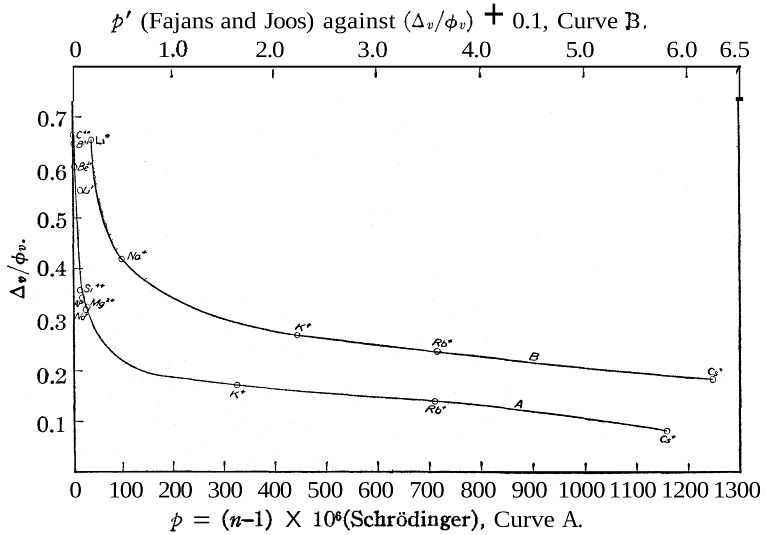

Fig. 3.

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[6] Schrodinger, Ref. 4, p. 66. The data for $(n-1) \times 10^6$ are used.

The ionic refraction of the alkali ions is also plotted against Δ_v/ϕ_v in Fig. 3, the Δ_v/ϕ_v values being increased 0.1 to prevent overlapping. It is obvious that the same sort of systematic relationship exists. The function Δ_v/ϕ_v is, therefore, a useful index to the polarizability of the ions.

Summary

1. The ionic potentials of the inert-gas type ions have been recalculated to volts and compared with ionizing potentials.

2. It is indicated that the valence electron of alkali and alkaline earth ions comes within the crystal radius with ions 0.3 Å. and 0.2 Å. larger than cesium and barium ions, respectively.

3. The ionic polarizability by light or by electrons varies systematically with the fractional difference between the ionic and ionizing potentials, which therefore may be used to estimate the polarizability.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE FRENCH BATTERY COMPANY, MADISON, WISCONSIN]

THE REACTIONS OF AMMONIA ON THE SYSTEM $ZnCl_2$–NH_4Cl–H_2O

BY RALPH FRIESS

RECEIVED APRIL 23, 1930 PUBLISHED AUGUST 5, 1930

The literature contains much information relating to the composition and preparation of the zinc–ammonium chloride double salts and the oxy and hydroxy forms as well, but little or no attention seems to have been given to the mechanism of the reactions, especially in relation to hydrogen-ion concentration.

It is the object of this investigation to study the formation of insoluble salts in aqueous solution where the ammonium chloride, zinc chloride, ammonia or ammonium hydroxide concentrations are varied. The actual experimental work covered the following ground: (1) determination of the PH of aqueous zinc chloride–ammonium chloride solutions in the range of solubility at 20°; (2) determination of the approximate quantity of ammonia which the solutions absorb to the point of formation of a permanent precipitate; (3) determination of PH of the supernatant liquors in equilibrium with these precipitates; (4) analysis of the precipitates obtained.

Experimental Procedure

The range of possible concentrations of zinc chloride-ammonium chloride in water at 20° (without supersaturation) was first shown graphically by plotting the aqueous solubilities of zinc chloride–ammonium chloride mixtures on triangular coordinate paper (Fig. 1). The solubility values were as determined by Meerburg.[1] Concentrations were selected to cover the entire range of possible solutions.

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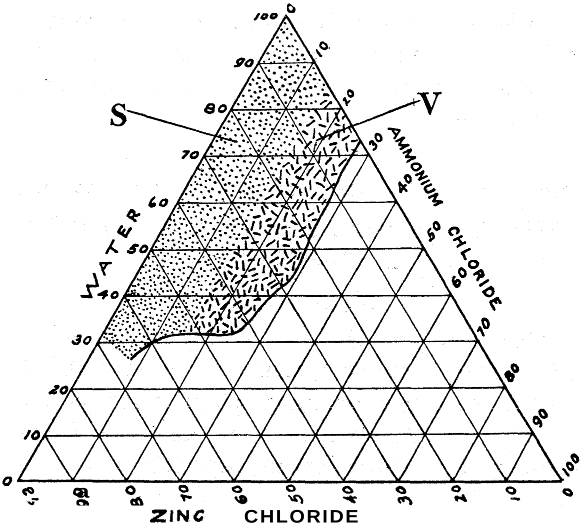
[1] Meerburg, Z. anorg. Chem., 37, 206 (1903).

The stock zinc chloride and ammonium chloride for these solutions were prepared as follows. (1) A stock solution of zinc chloride was prepared from the technical fused salt and the solution allowed to stand for several days, after which it was filtered through asbestos fiber. It analyzed 67.88% $ZnCl_2$ and 0.077% Fe. (2) The ammonium chloride was obtained by recrystallizing the white commercial 99% grade and drying for twenty-four hours at 105°. The recrystallized salt showed no trace of iron with ammonium sulfocyanate reagent.

The solutions (160 g. of each) were carefully made up from the stock zinc chloride solution, recrystallized ammonium chloride and distilled water. They were not subsequently analyzed.

The *P*H measurements were made with the hydrogen electrode and a Type K Leeds and Northrup potentiometer.



V, $ZnCl_2 \cdot 2NH_3$; S, basic salt.

Fig. 1.—Showing solubility range of $ZnCl_2$–NH_4Cl mixtures in water at 20°, and areas in which ammonia precipitates $ZnCl_2 \cdot 2NH_3$ and the basic salt.

It was first attempted to pass measured quantities of pure gaseous ammonia into the solutions, but this was found impracticable due to the rapid clogging of the end of the delivery tube with insoluble salts. The introduction of ammonia was finally effected by bubbling definite volumes of carbon dioxide-free air through a large volume of ammonia water maintained at 20°, thence through glass wool vapor traps and finally into the solutions. The apparatus was calibrated, i. e., the ammonia content of a definite volume of the air passed through this train was determined after each three or four runs. This method was quite crude but was found to be within 10% accuracy.

The various solutions tried absorbed all ammonia passed into them; i. e., no appreciable quantity of ammonia escaped as determined by leading the air through a known quantity of standard acid solution after passing through the solutions studied.

The introduction of ammonia was stopped when the first trace of a permanent precipitate occurred. The solutions, which were in Erlenmeyer flasks, were stoppered and allowed to remain for at least twenty-four hours before *P*H measurements were made on the supernatant liquor by the method mentioned heretofore, The solutions were separated from the precipitates by filtering through an asbestos fiber layer in a Gooch crucible. Each precipitate was washed with from 15 to 25 cc. of 95% alcohol, followed by 10 cc. of ether. They were then dried at 100° for two to four hours. The precipitates obtained from the more concentrated solutions were removed from the crucible, suspended in about 20 cc. of 95% alcohol and again filtered. There was no trouble in separating the precipitates from the asbestos fiber as the washed and dried precipitates "poured" out quite readily after gently tapping them loose with a glass rod. The weight of the precipitate obtained was 2 to 3% of the total weight of solution taken. No analysis was made of the supernatant liquors after the addition of ammonia.

Results

Table I shows the composition of the solutions before adding ammonia, the PH before and after the addition of ammonia, grams of ammonia absorbed up to the point of the first permanent precipitate, analysis of precipitate and nature of precipitate.

TABLE I

COMPOSITION AND PH OF SOLUTIONS, AMMONIA ABSORBED AND ANALYSIS OF PRECIPITATES

No.	$ZnCl_2$, %	NH_4Cl, %	H_2O, %	PH	PH after adding NH_3	G. of NH_3 added per 100 g. of soln	Analysis of ppts. Zn, %	Cl, %	NH_3, %	Precipitate
1	0	26.9	73.1	4.66	..	0	...	...	...	None
2	5.0	15.0	80.0	4.60	6.19	.9	38 22	41.87	19.86	$ZnCl_2\cdot 2NH_3$
3	5.0	5 0	90.0	4.93	5.41	.3	58.10	15.45	...	Basic
4	15.0	27.6	57.4	4.43	5.52	.7	38.37	41.63	20.00	$ZnCl_2\cdot 2NH_3$
5	15.0	20.0	65.0	4.34	5.54	1 0	38.19	41.89	19.80	$ZnCl_2\cdot 2NH_3$
6	15.0	10 0	75.0	4.48	5.56	1.3	51.72	24.01	7.10	Basic
7	15.0	0	85.0	4.97	4.82	0[a]	54.70	...	...	Basic
8	25.0	15.0	60.0	4.09	5.07	1.2	38.09	41.91	...	$ZnCl_2\cdot 2NH_3$
9	26.0	29.0	45.0	4.29	5.02	0.6	38.21	41.79	19.53	$ZnCl_2\cdot 2NH_3$
10	30.0	20.0	50.0	3.86	5.04	1.2	38.58	41.54	19.79	$ZnCl_2\cdot 2NH_3$
11	30.0	5.0	65.0	4.03	4.64	0.6	61.14	13.37	.09	Basic
12	40.0	20.0	40.0	3.22	4.66	1.6	38.65	41.61	19.68	$ZnCl_2\cdot 2NH_3$
13	40.0	10.0	50.0	3.22	4.33	1.2	56.65	17.43	3.02	Basic
14	43.2	26.0	30.8	3.08	4.59	2.1	38.26	41.86	19.88	$ZnCl_2\cdot 2NH_3$
15	50.0	10.0	40.0	2.39	3.67	1.4	54.65	19.46	2.93	Basic
16	53.2	14.5	32.3	1.89	3.43	1.8	55.74	18.32	3.13	Basic
17	60.0	5.0	35.0	1.27	2.67	1.3	57.85	15.99	0.39	Basic
18	60.0	0	40.0	1.44	2.46	0.2	57.55	15.13	0.20	Basic
19	66.6	7.9	25.5	..	..	...	...	...	...	...
20	62.0	9.0	29.0	1.05	2.47	1.1	48.44	32.26	6.60	Basic
21	33.3	0	66.7	4.05	..		...	...	. . . .	
22	50.0	0	50.0	2.71	.	...	...	...	. . . . . .	

[a] Precipitate formed on standing without addition of ammonia.

Table II shows the composition of the basic precipitates recalculated on the basis of zinc, chlorine and oxygen only. It was assumed that the ammonium ion was present as ammonium chloride uncombined with the other constituents. There is also a possibility of free zinc chloride being present. The basicity was determined by dissolving a 0.2-g. sample in an excess of normal sulfuric acid and titrating back with half normal sodium hydroxide. The basicity was computed as "O."

TABLE II

COMPOSITION OF BASIC PRECIPITATES RECALCULATED ON BASIS OF Zn, Cl AND O ONLY

Precipitate no.	Zn, %	Cl, %	O, %	Moles per 100 grams Zn	Moles per 100 grams Cl	Moles per 100 grams O
6	72.30	12.90	14.80	1.10	0.36	0.93
11	70.90	15.27	13.83	1.08	.43	.86
13	71.51	14.05	14.44	1.09	.40	.90
15	69.68	17.02	13.30	1.05	.48	.83
16	71.22	15.07	13.72	1.09	.43	.86
17	69.12	18.14	12.74	1.06	.51	.80
18	69.47	17.77	12.76	1.06	.50	.80
20	65.03	24.85	10.12	0.99	.70	.63
Average[a]				1.08	.44	.85

[a] Values for precipitate No. 20 are omitted from the average due to their considerable deviation from the other values.

Figure 1 shows the range of possible concentrations of zinc chloride and ammonium chloride in water at 20° (without supersaturation) and also the areas in which $ZnCl_2 \cdot 2NH_3$ and the basic precipitate are obtained when ammonia is added.

Discussion

The data show that two kinds of precipitates were formed, *viz.*, $ZnCl_2 \cdot 2NH_3$ and basic zinc chloride.

The identity of the $ZnCl_2 \cdot 2NH_3$ compound is unmistakably shown by (1) the analysis, which checks closely with the theoretical 38.37% Zn, 41.63% Cl and 20.00% NH_3, (2) definite crystal form, (3) milky appearance when treated with water and (4) the evolution of ammonia with no ammonium chloride fumes when gently heated, leaving fused zinc chloride.

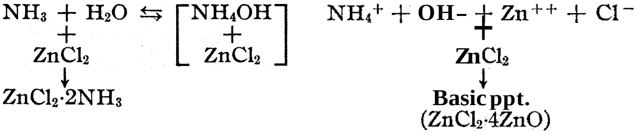
All basic precipitates when heated gave off water vapor and some ammonium chloride fumes, after which the mass became sticky, congealing to a hard vitreous mass on cooling. A mixture of zinc oxide and zinc chloride in about equal proportions acted in the same way. This combination is sometimes used as a cement.

A study of the results of analysis of the basic precipitates and the conditions of their formation indicates that they consist of a basic zinc chloride with the admixture of free zinc chloride and ammonium chloride. The data in Table II were obtained by deducting the percentage of ammonium and the theoretical percentage of chlorine combined with it to form ammonium chloride, then computing the percentage composition with the basicity figured as oxygen. It was not possible to determine the admixed zinc chloride. The results, however, show closer agreement than the original analysis but there is still considerable variation. However, the average moles of zinc, chlorine and oxygen per 100 g. of basic precipitate (Table II) point to the formula $ZnCl_2\cdot 4ZnO$.

The experimental data show that if the ammonium chloride content is 15% or above, regardless of the zinc chloride content (above at least 5%), the compound $ZnCl_2\cdot 2NH_3$ is precipitated by adding ammonia. Below 15% ammonium chloride the basic compound is thrown down.

Obviously a preponderance of dissolved gaseous ammonia would favor the formation of $ZnCl_2\cdot 2NH_3$, while excessive hydroxyl ions would throw the reaction in favor of $ZnCl_2\cdot 4ZnO$, or some other similar basic compound.

The reactions can be represented by the chemical equations



$$\begin{array}{ccc}
NH_3 + H_2O \leftrightarrows & \begin{bmatrix} NH_4OH \\ + \\ ZnCl_2 \end{bmatrix} & NH_4^+ + OH^- + Zn^{++} + Cl^- \\
+ & & + \\
ZnCl_2 & & ZnCl_2 \\
\downarrow & & \downarrow \\
ZnCl_2\cdot 2NH_3 & & \text{Basic ppt.} \\
 & & (ZnCl_2\cdot 4ZnO)
\end{array}$$

The addition of ammonium chloride drives equilibrium to the left since ammonium ions from ammonium chloride repress the ionization of ammonium hydroxide. When the ammonium chloride content is less than 15%, the hydroxyl ions can be made sufficiently concentrated (by addition of ammonia, forming ammonium hydroxide) to exceed the solubility product for the basic zinc salt ($ZnCl_2\cdot 4ZnO$).

Conclusions

When ammonia is added to zinc chloride–ammonium chloride solutions at 20°, $ZnCl_2\cdot 2NH_3$ is precipitated when the ammonium chloride content is about 15% or above, and a basic precipitate, probably $ZnCl_2\cdot 4ZnO$, is precipitated when the ammonium chloride content falls below 15%.

The mechanism of the reaction in the system $NH_3{-}ZnCl_2{-}NH_4Cl{-}H_2O$ is explained by the concentrations of the various constituents and the effect which ammonium chloride has upon the extent of ionization of these constituents.

MADISON, WISCONSIN

[Contribution from Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils]

EQUILIBRIA IN THE AMMONIUM CARBAMATE–UREA–WATER–AMMONIA SYSTEM

By H. J. Krase[1] and V. L. Gaddy

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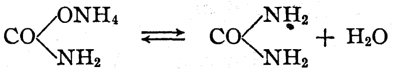
The present expansion of synthetic ammonia production in this country has stimulated interest in the production of new nitrogen carriers that can be used for agricultural purposes. In this regard, urea is a most promising compound. It has a high nitrogen content, it is readily hydrolyzed in the soil, and it is easily assimilated by plants. Then too, it is important as a starting point for organic syntheses, and for the production of condensation products of urea and formaldehyde. Undoubtedly as the cost of production of urea is reduced, other uses will be developed.

Historical.—The first synthesis of urea from carbamate was probably accomplished by Bassarow[2] in 1870, by heating ammonium carbamate in sealed glass tubes between 130 and 140°. He pointed out that an equilibrium is established between the carbamate dehydration reaction and the hydrolysis of urea with the water liberated according to the equation[2]



$$\mathrm{CO}\begin{matrix}\diagup ONH_4\\ \diagdown NH_2\end{matrix} \rightleftharpoons \mathrm{CO}\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} + H_2O$$

Bourgeois[3] later investigated the same reaction using, in addition to ammonium carbamate, the carbonate, the sesquicarbonate and the bicarbonate, heating in each case to 130°. The yields of urea varied from 1.5 to 9.52%.

Fichter and Becker[4] have studied this reaction from the standpoint of the effect of temperature, loading density and added water on the equilibrium. They found that the maximum conversion was reached at a temperature of 135° and also that the conversion increased with the loading density or ratio of the weights of the materials to the total volume of the reaction vessel. Added water caused the conversion to fall off, so that the best conversion was obtained with pure ammonium carbamate.

Further work on the conversion of carbamate was carried out by N. W. Krase and V. L. Gaddy.[5] They concluded that because of the endothermicity of the urea formation reaction, the use of a higher temperature would result in a higher yield; that is, they were unable to find an optimum temperature such as reported by Fichter and Becker. The other findings

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[1] Present address: Swann Research, Inc., Anniston, Ala.

[2] Bassarow, *J. prakt. Chem.*, [2] 1, 283 (1870).

[3] Bourgeois, Bull. *soc. chim.*, [3] 7, 48 (1892); 17, 474 (1897).

[4] Fichter and Becker, Ber., 44, 3473 (1911).

[5] N. W. Krase and V. L. Gaddy, J. Ind. *Eng. Chem.*, 14, 611 (1922).

of Fichter and Becker with regard to the effects of loading density and added water on the equilibrium were, however, in general, substantiated by the later work. N. W. Krase and V. L. Gaddy in reporting the effect of water on the urea conversion gave data which by extrapolation to dry carbamate indicated a conversion to urea at 150° of about 44%. Matignon and Fréjacques[6] in a study of the same problem, found a maximum conversion of 43.3% at 145°. In general, it may be said that the equilibrium in the carbamate dehydration reaction at 150° is of the order of 44% of the ammonia converted to urea. No one, to our knowledge, has been able to show a higher conversion starting with ammonium carbamate alone.

In 1917 Fichter, Steiger and Stanisch[7] reported some work in which they heated ammonium carbamate with ammonia. They concluded that in the absence of water, ammonia exerts a beneficial influence only when moderate amounts are used. With larger amounts of ammonia the conversion to urea was found to be adversely affected. They explained the beneficial effect of a moderate amount of ammonia as being due to the prevention of vaporization of carbamate, which increased the amount of salt in the liquid phase. Obviously, an increase in the loading density would have a similar effect. They concluded that a secondary reaction takes place in the presence of large excess of ammonia resulting in the formation of guanidine. In the following work we have tested some of our urea formed in the presence of as much as 300% excess ammonia and have discovered no guanidine.

The possibility of using dehydrating agents to remove the water formed in the reaction has been considered by Matignon and Fréjacques. They performed experiments using dehydrated magnesium sulfate in the liquid and in the gas phase and using calcium chloride in the gas phase. In all cases a conversion lower than that obtained by heating carbamate alone was obtained, probably because of the reaction with the dehydrating agent. To date no satisfactory dehydrating agent for this reaction has been reported.

Preliminary Experiments

The extent to which water enters into the reverse reaction is illustrated in the following three experiments. They were performed in a lead-lined steel bomb, of approximately 100 cc. capacity, heated in an oil-bath at 150° for three and one-half hours. The customary 40 odd per cent. yield was obtained in Expt. 1, in which carbamate alone was heated. Experiments 2 and 3 were designed to show the effect on the equilibrium if the water formed under normal conditions had been removed from the reaction zone. This was accomplished in Expt. 2 by loading the bomb with carbamate and urea only, and in Expt. 3 by loading with urea and a small

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[6] Matignon and Fréjacques, Bull. *soc. chim.*, 31,807 (1922).

[7] Fichter, Steiger and Stanisch, *Verhand. der Natur. Gesell. Basel, 28,* 66 *(1917).*

quantity of water. The quantities used were such that in each case the deficiency of water in the system equaled the amount of water that would have been produced in the normal equilibrium. The results of these experiments are recorded in Table I, the last column of which indicates the percentage of carbamate converted to urea or the percentage of urea left undecomposed. Comparison of Expts. 2 and 3 shows that the ordinary test for an equilibrium condition was fulfilled since the conversion approached from the carbamate side of the reaction was also reached from the urea–water side.

TABLE I[a]

RESULTS OF EXPERIMENTS

Experiment	Charge before heating	Calcd. charge after heating	Conversion to urea, %
1	78 g. carbamate	44.6 g. carbamate 25.8 g. urea 7.7 g. H_2O 78.1 g. total	43.0
2	44.5 g. carbamate 25.8 g. urea 70.3 g. total	27.9 g. carbamate 38.6 g. urea 3.80 g. H_2O 70.3 g. total	64.2
3	60 g. urea 10.3 g. H_2O 70.3 g. total	27.00 g. carbamate 39.40 g. urea 3.90 g. H_2O 70.30 g. total	65.3

[a] These experiments were performed by the late C. D. Garby.

The above experiments prove what might be deduced *a priori* from a consideration of the mass law. In order to obtain such increased yields of urea with carbamate as the starting point, it is necessary to find an efficient dehydrating agent which otherwise does not react with the melt and which can be removed readily after the reaction is complete. Ammonia and carbon dioxide appeared most promising for this purpose, since they could not further react with the carbamate or the urea and could be readily recovered and utilized again.

Apparatus and Method

Two duplicate reaction bombs were made of Rezistal 4, a high chrome-iron alloy which had been found to be fairly resistant to the action of the melt. They were approximately 9 cm. in outside diameter and 17 cm. high, having a cavity approximating 100 cc. in volume. Each was provided with a Geophysical type valve, screwed into the plug which was forced onto a gasketed seat by a heavy annular nut. Loading was accomplished by weighing out the pure dry carbamate or urea, introducing it into the bomb, adding the equivalent amount of water and then screwing down the closing plug carrying the valve. The anhydrous ammonia or the carbon dioxide was then weighed in a steel weighing pipet, the large bomb cooled in an ice-bath and the pipet connected to the valve on the bomb. In a short time all of the liquid ammonia or carbon dioxide had run into the bomb. The two bombs, one loaded with carbamate + ammonia, the other with urea + water + ammonia, were heated to 100° in boiling water, and then placed side by side in the bromobenzene vapor-bath shown in Fig. 1. Heating was continued for twenty-four hours, the bombs were removed and placed in a water-bath maintained at 60°. The valves were then cracked and the ammonia distilled into water, where it was determined by titrating an aliquot part. Following distillation of the excess ammonia the bombs were cooled to 15°, the tops removed and the charges washed out and made up to volume. These solutions were then analyzed by determining the total nitrogen by the Kjeldahl method, the urea by the urease method and the ammonia by the direct titration of an aliquot part.

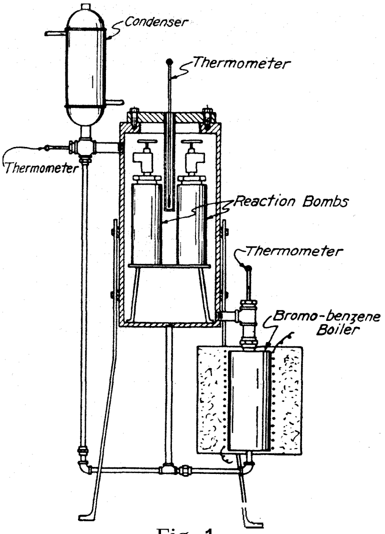

Fig. 1.

Results

The total nitrogen loaded either as carbamate and ammonia or as urea and ammonia varied between 11 and 30 g. in each bomb. The difference between the nitrogen loaded into the bombs at the beginning of an experiment and the nitrogen later found by analysis, was taken as lost and, of course, included errors in weighing and leaks during the run. Probably most of this nitrogen was lost as ammonia from the vapor phase through leaks in the valve and gasket. The actual loss in all of the successful experiments was in the neighborhood of 1 to 7% of the nitrogen loaded. For this reason the calculation of the excess ammonia in each bomb was made on the basis of the total nitrogen as found on analysis and is expressed as percentage of the ammonia loaded as carbamate or as urea, taking into consideration the purity of the salt, which in all cases was in the neighborhood of 99.9% for the urea and 99.4% for the carbamate.

The percentage conversion of the carbamate to urea and the percentage of urea undecomposed by the reverse reaction are expressed as percentage conversion of carbamate ammonia (in Table II) and in the graph of results. These quantities are calculated on the basis of the weights of carbamate or

TABLE II

EXCESS AMMONIA (TEMP., 154–155.6°)

Expt.	Starting materials	Ammonia in excess of carbamate ammonia, %	Conversion of carbamate ammonia to urea, %
1	Carbamate + ammonia	0	43.5
2	Urea + water + ammonia	0	44.0
3	Urea + water + ammonia	19.5	49.7
4	Urea + water + ammonia	23.0	47.7
5	Carbamate + ammonia	23.0	49.5
6	Urea + water + ammonia	23.0	50.2
7	Carbamate + ammonia	23.0	51.5
8	Carbamate + ammonia	26.3	53.0
9	Carbamate + ammonia	45.2	58.2
10	Urea + water + ammonia	45.2	58.7
11	Urea + water + ammonia	53.2	63.5
12	Carbamate + ammonia	63.0	63.5
13	Carbamate + ammonia	76.5	67.0
14	Urea + water + ammonia	82.5	67.0
15	Urea + water + ammonia	89.5	64.0
16	Carbamate + ammonia	96.0	70.5
17	Urea + water + ammonia	173.3	80.2
18	Urea + water + ammonia	210.0	82.5
19	Carbamate + ammonia	222.0	81.5
20	Urea + water + ammonia	279.0	85.2
21	Carbamate + ammonia	280.5	81.0

urea initially loaded into the bomb. The percentage of excess ammonia, based on the ratio of the nitrogen present as ammonia nitrogen to the nitrogen in combination as carbamate and urea is represented by the abscissa in Fig. 2.

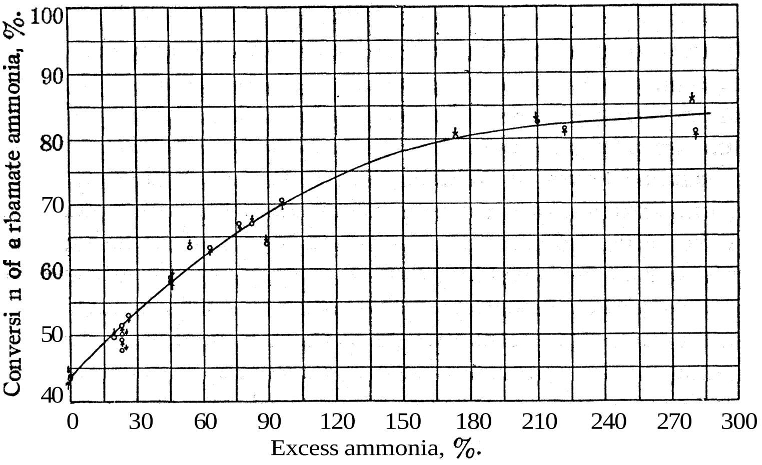

Fig. 2.

Each point on the graph is marked by means of an arrow to indicate whether the equilibrium is approached from the increasing or decreasing urea side of the reaction. The temperature in the experiments varied between 154 and 155.6°.

Excess Carbon Dioxide.—The conversion obtained with no excess ammonia is very close to 44%. This is in agreement with the finding of other investigators as already noted. Several experiments with an excess amount of carbon dioxide were also made. Since they are not shown on the graph they are given in Table III.

TABLE III

EXCESS CARBON DIOXIDE (TEMP., 155.6')

Expt.	Starting materials	Carbon dioxide, % of combined CO_2 in starting material	Conversion to urea
1C	Carbamate + carbon dioxide	97.0	44.35
2C	Urea + water	100.0	44.0
3C	Carbamate + carbon dioxide	61.2	44.3
4C	Urea + water + carbon dioxide	61.2	45.7

Conclusion

The experimental results show that an excess amount of ammonia over that combined as carbamate acts as a dehydrating agent, removing the water from the active mass, thus preventing its reaction with urea and thereby shifting the equilibrium toward the urea side. Carbon dioxide does not show this effect. The slope of the conversion curve at 300% excess ammonia is such that a complete dehydration is not to be expected with more ammonia, under the conditions here considered.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE IODIMETRIC DETERMINATION OF SMALL AMOUNTS OF ZINC

BY H. ARMIN PAGEL AND OLIVER C. AMES

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It has been shown by Spacu[1,2] and his co-workers, that zinc can be very accurately determined by precipitating the zinc as zinc pyridine thiocyanate, which may be weighed as such or ignited and weighed as zinc oxide. By employing special apparatus Spacu and Ripan[3] extended their method to the gravimetric determination of as low as 12 mg. of zinc. Unlike most very insoluble zinc compounds, zinc pyridine thiocyanate precipitates in a distinctly crystalline form which transfers and filters perfectly. The precipitate is definite in composition and has the formula,

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[1] G. Spacu, Z. *anal. Chem.*, 64,338 (1924).

[2] G. Spacu and J. Dick, *ibid.*, 73, 356 (1928).

[3] G. Spacu and R. Ripan, *ibid.*, 64,338 (1924).

$ZnPy_2(SCN)_2$. Apparently no one has attempted the iodimetric determination of the thiocyanate in this precipitate as the basis of the volumetric determination of small amounts of zinc.

In slightly alkaline solution iodine reacts with thiocyanate according to the reaction

$$NCS^- + 4I_2 + 8OH^- \longrightarrow SO_4^= + 7I^- + 4H_2O + ICN \qquad (A)$$

Upon acidification the iodocyanogen again reacts instantly and quantitatively with iodide to form iodine and cyanide, giving the final quantitative relation

$$NCS^- + 3I_2 + 4H_2O \longrightarrow SO_4^= + 8H^+ + 6I^- + CN^- \qquad (B)$$

On the basis of the above reactions, it was found in this Laboratory that alkali thiocyanate can be very accurately determined iodimetrically by adding a moderate excess of standard iodine solution to a thiocyanate solution made alkaline with the proper amount of borax, and then acidifying the reaction mixture and titrating the excess iodine with standard thiosulfate, using starch as indicator. A. Schwicker,[4] who also recently worked on the iodimetric determination of alkali thiocyanates, states that borax is unsatisfactory as a buffer for the oxidation reaction. His failure to obtain satisfactory results was undoubtedly due to the use of an insufficient amount of borax.[5]

Since alkali thiocyanate can be accurately determined by the method referred to above, the same method was applied directly to the zinc pyridine thiocyanate precipitate. In order to establish this, about a gram of the precipitate was specially prepared by adding the calculated amounts of the precipitating agents to a very dilute boiling hot solution of zinc sulfate and allowing the solution to cool slowly without disturbance. In this way large needle-like crystals (about 2 cm. in length) were obtained. These were filtered and washed several times with anhydrous methyl alcohol and then dried at room temperature in vacuo. Weighed portions of this material were dissolved in hot water, and borax was then added and the mixture boiled to expel the pyridine. After cooling, the determination was carried out according to the principle stated above, for the determination of alkali thiocyanate. The removal of the pyridine by boiling in the presence of borax insured a very sharp end-point in the residual titration with thiosulfate. In the presence of borax the zinc is precipitated as *a* flocculent basic zinc borate. It might seem that this precipitate would occlude considerable thiocyanate. This, however, is not the case, for the results given in Table I show excellent agreement with the theoretical.

Apparatus and Reagents

Bureau of Standards certified burets, pipets and volumetric flasks were used in all precision measurements. A 25-cc. buret was used for the

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[4] A. Schwicker, Z. *anal. Chem.*, 77,278 (1929).

[5] Pagel and Ames, THIS JOURNAL, 52,2698 (1930).

residual titration with thiosulfate. Conductivity water prepared with a large specially constructed all-pyrex still was used throughout. Highest purity chemicals were used with the exception of borax ($Na_2B_4O_7 \cdot 10H_2O$) which was Mallinckrodt C. P. grade. Samples of the recrystallized material, however, gave identical results. Standard zinc solutions were prepared from U. S. Bureau of Standards stick zinc (Sample No. 43a) containing less than 0.01% total of detected impurities. Accurately weighed portions of this zinc were placed in a 2-liter volumetric flask with a slight calculated excess of dilute sulfuric acid. While the zinc was dissolving the flask was kept in cold water to insure very slow reaction in order to eliminate any losses due to spray. Pipetted portions of the standard zinc solution were used in the determinations. Where very small amounts of zinc were desired, aliquot parts of the standard solution were again accurately diluted, and pipetted portions of the latter again taken. Standard 0.1 N potassium iodate solution (used as a source of free iodine) was prepared directly by dissolving and diluting the calculated weight of the pure dried salt. The ratio of the 0.1 N thiosulfate to the iodine liberated from the iodate was determined under the same conditions that were present in the actual determinations. Temperature corrections for the standard solutions were taken into account.

Experimental

Weighed portions of the pure zinc pyridine thiocyanate were transferred into a 500-cc. wide-mouthed conical flask. About 125 cc. of water was added and the contents of the flask heated nearly to boiling, until the precipitate dissolved. Six grams of borax was then added and the mixture gently boiled for about ten minutes. After allowing to cool somewhat, the flask was stoppered with a clean rubber stopper (previously cleaned thoroughly by boiling in dilute alkali) and thoroughly cooled with tap water. In a second 500-cc. flask, a 50-cc. pipetted portion of the iodate solution was treated with 2 g. of potassium iodide and 10 cc. of 1 N hydrochloric acid. The cold borax reaction mixture was then immediately transferred, and thoroughly rinsed with water, into the flask containing the liberated iodine. After rinsing down any drops on the sides, the flask was stoppered and allowed to stand for ten or fifteen minutes to insure complete oxidation. The total volume at this stage was about 150 cc. Ten cc. of 6 N hydrochloric acid was then added and the excess iodine immediately slowly

TABLE I

RESULTS WITH PURE $ZnPy_2(SCN)_2$

$ZnPy_2(SCN)_2$, g.	Iodine, 0.1000 N Calcd., cc.	Reduced, cc.	Error, %
0.0849	30.00	30.02	+0.1
.0849	30.00	30.04	+ .1
.0900	31.80	31.83	+ .1

titrated to almost colorless with standard thiosulfate before adding starch indicator.

The following procedure and technique was found to give very satisfactory results for the determination of various small quantities of zinc, ranging from **3** to **33** mg. in a volume of 100 cc. The technique is not difficult; nevertheless, every detail given is essential for accurate results.

One gram of solid potassium thiocyanate is dissolved in the zinc solution, followed by 1 cc. of pyridine, which is added drop by drop while stirring. This is then allowed to stand for one hour, with occasional stirring to insure complete precipitation of the zinc in the supernatant liquid. During this time the temperature of the precipitation mixture should not be allowed to rise above 20°. Filtration is then effected by using a snugly fitting disk of filter paper in a clean 25-cc. capacity Gooch crucible. This disk of paper, of such size that the edges will be slightly turned up against the inside walls of the crucible, is best prepared by tracing the circumference with a knife and tearing along the mark to produce *a* smoothly frayed edge. The crucible is forced into a rubber ring (Bailey crucible holder) until the bottom protrudes at least 1 cm. through the ring. The ring is then placed in a clean funnel fitted into a suction flask. A transfer solution is prepared by dissolving 10 g. of potassium thiocyanate and 10 cc. of pyridine in a liter of water. After wetting the filter with this solution and sucking down firmly, the precipitate is filtered with gentle suction and quantitatively transferred with the transfer solution. The precipitate is then washed with not more than 10 cc. of a solution of anhydrous ether containing 1% of pyridine by volume, cooled to 20° or lower. The greater part of the ether wash solution should be directed down the sides of the crucible in a very fine stream. The crucible is then removed and the outside wiped clean with a damp towel. The crucible is then inverted over a 500-cc. wide-mouthed conical flask, and the filter paper together with nearly all of the precipitate is dislodged by thrusting a fine wire through the bottom of the crucible. The crucible is washed thoroughly with boiling water and the volume of solution increased to approximately 150 cc. This is heated until the precipitate is completely dissolved, ignoring the slight amount of flocculent zinc hydroxide which may form. After adding 6 g. of borax, the determination is completed according to the procedure given above, in the analysis of the weighed portions of the pure precipitate. A minimum excess of 5 cc. of 0.1 N iodine, over that required for reaction **(A),** is essential for the complete oxidation of the thiocyanate in ten minutes, in a volume of 150 cc. This excess is estimated with sufficient accuracy by comparing the color of the oxidation mixture (after standing for two minutes) with the color produced by the iodine, liberated under the same conditions, from 5 cc. of 0.1 N iodate in 150 cc. of water. If the excess iodine found is less than that **specified,** a second pipetted portion of iodate is treated as before and the reaction mixture is quantitatively added to the iodine solution. An additional gram or two of powdered borax is then added to compensate for the increased volume. Obviously, standard iodine solution may be used throughout in the procedure. A blank of the thiocyanate adsorbed on the filter paper and crucible must be determined. This is done by preparing a crucible as previously described and washing with the transfer solution, followed with the ether wash, as in the actual determination. The thiocyanate on the filter paper is determined exactly as in the regular determination, except that a 10-cc. portion of iodate is sufficient. Table II shows the results obtained with pure zinc sulfate solution.

TABLE II

ANALYTICAL RESULTS

Zinc taken, mg.	Iodine, reduced, cc of 0.1000 N	Zinc found, mg.	Error, mg.	Error, %
17.98	32.91	17.93	−0.05	−0.3
17.98	32.93	17.94	− .04	− .2
17.98	33.01	17.98	.00	.0
17.98	33.09	18.03	+ .05	+ .3
8.21	15.10	8.23	+ .02	+ .2
8.21	15.00	8.17	− .04	− .5
3.286	5.95	3.241	− .045	−1.4
3.286	5.97	3.252	− .034	−1.0
3.286	5.96	3.247	− .039	−1.2

Table III shows the effect of salts which are usually present at this stage of an analytical determination.

TABLE III

EFFECT OF SALTS

Zinc taken, mg.	Salts added, grams	Iodine reduced, cc. of 0.1000 N	Zinc found, mg.	Error, mg.	Error, %
32.86	2, Na_2SO_4	60.09	32.73	−0.13	−0.4
17.98	2, Na_2SO_4	32.98	17.97	− .01	.0
17.98	2, Na_2SO_4	32.91	17.93	− .05	− .3
16.43	4, Na_2SO_4	30.15	16.42	− .01	.0
16.43	4, Na_2SO_4	30.23	16.47	+ .04	+ .2
8.99	2, Na_2SO_4	16.46	8.97	− .02	− .2
8.99	2, Na_2SO_4	16.56	9.02	+ .03	+ .3
16.43	1, $NaNO_3$	30.19	16.45	+0.02	+ .1
16.43	2, $NaNO_3$	30.10	16.40	− .03	− .2
16.43	1, NaCl	29.92	16.30	− .13	− .8
16.43	4, NaCl	29.58	16.11	− .32	−1.9
8.21	4, NaCl	14.90	8.12	− .09	−1.1
32.86	1, NaCl 1, Na_2SO_4	59.59	32.46	− .40	−1.2

It is apparent that chloride interferes seriously, while sulfate or nitrate does not. Spacu and Dick[2] have shown that ammonium salts give low results, and that magnesium and the alkaline earths do not interfere.

Copper, cadmium, cobalt, nickel and manganese interfere, since these form corresponding insoluble pyridine thiocyanate precipitates.

The amount of thiocyanate remaining adsorbed on the crucible and filter paper after the final ether wash was found to be practically independent of a preliminary wetting with sodium sulfate solution, and the amount of ether wash. A series of blanks using Whatman No. 40 ashless filter paper showed consistent values of 0.40 cc. (±0.01) of 0.1 *N* iodine.

Summary

The iodimetric determination of small amounts of zinc, precipitated as zinc pyridine thiocyanate, has been developed. Data and the details of the procedure and technique have been included.

LINCOLN, NEBRASKA

[CONTRIBUTION NO. 631 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

RAPID REACTIONS.
THE VELOCITY AND HEAT EFFECTS INVOLVED IN THE NEUTRALIZATION OF SODIUM DICHROMATE BY SODIUM HYDROXIDE[1]

BY VICTOR K. LA MER AND CHESTER L. READ

RECEIVED MAY 1, 1930 PUBLISHED AUGUST 5, 1930

1. Introduction

Various investigators have endeavored to study some of the more rapid reactions but little has been accomplished in this field until comparatively recently. Abegg and Neustadt[1a] tried to follow the reaction between H^+ and OH^- in alcoholic solutions at low temperatures. It is quite probable that the reported time of the reaction, one-half to two minutes, was the time required for the solutions to mix at that temperature. Benedicks[2] used similar solutions at room temperature and attempted to follow the rate of reaction by conductivity methods. Round holes were cut in two glass plates and each hole was fitted with an electrode. One of the reacting solutions was placed in each of the cavities and the plates were moved so that the holes were rapidly brought opposite each other. The conductivity of the resulting solution was recorded continuously by mechanical methods. It was found that two-tenths of a second was required for complete mixing of the solutions, while the reaction reached completion in a much shorter time.

The first comprehensive study of a rapid reaction was made by Hartridge

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[1] This paper is constructed from a Thesis submitted by Chester L. Read in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Columbia University.

[1a] Abegg and Neustadt, *Z. Elektrochem.*, 14, 2 (1908).

[2] Benedicks, *Z. physik. Chem.*, 70, 12 (1910).

and Roughton[3] when they applied their flowing stream method to a reaction involving hemoglobin. The principle of the method consisted in causing the solutions whose reaction is to be studied to come together at high velocity in a mixing chamber where they are rapidly and completely mixed. The resulting solution then passes through a reaction tube where the progress of the reaction is observed. With constant velocity maintained through the tube, the time required for the mixed solution to reach a given point is constant and consequently the reaction is always in the same state when the solution reaches this point. Various methods may be used to follow the progress of the reaction; in most of the work reported by Hartridge and Roughton the spectroscope was used. In their most highly developed apparatus, the first reading could be taken $^1/_{6000}$ second after mixing. Although most of their work was along biological lines, the reaction between 0.1 normal solutions of hydrochloric acid and sodium hydroxide was studied and found to be complete in less than 0.001 second.[4]

Saal[5] used an apparatus of this type applying conductivity and e. m. f. methods to follow the reactions. He attempted a survey of the different types of reactions taking place between electrolytes and concluded that "ionic reactions in which there is no change of charge and in which no secondary reactions having a fundamental influence on the ion or molecule occur, are complete to 1% within 0.004 second" and that "oxidation and reduction reactions are usually slow."

In this research, the apparatus used was similar to that of Hartridge and Roughton except that the reactions were followed by means of thermocouples which measured the temperature change due to the heat of reaction evolved.

2. Apparatus

A schematic diagram of the apparatus is given in Fig. 1. Air, at constant pressure, is applied to the two sets of bottles C and D through the regulating valve A. The applied pressure is given by the manometer B. The two solutions are forced through glass tubes to the mixing apparatus E. Detailed views of the mixing apparatus are given in Fig. 2. It consists of two square gold-plated brass plates which are bolted together. Each plate contains a circular header, I and J, of square cross section, the outer diameter being 85 mm., the inner 45 mm. and the depth 15 mm. Each header is fed by two tubes; solution from bottles C and C′ enters header I by the tubes G and G′ while

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[3] Hartridge and Roughtou, (a) *Proc. Roy. Soc.*, (London) **A104,** 376 (1923); (b) *Proc. Camb. Phil. Soc.*, 22, 426 (1925); (c) *ibid.*, 23, 450 (1926).

[4] The continuous flow principle of calorimetry has been employed previously by Pratt, *J. Franklin Inst.*, 185, 663 (1918), for the determination of heats of dilution of aqueous solutions and by Keyes and Dickinson [Thesis, Massachusetts Institute of Technology, 1917, referred to by Keyes, Gillespie and Mitsukuri, THIS JOURNAL, 44, 707 (1922)] for the determination of heats of neutralization. Bray and Livingston, *ibid.*, 50, 1654 (1928), have also employed a flowing stream method but for the very much slower reaction between hydrogen peroxide and bromine.

[5] Saal *Rec. trav. chim.*, **47,** 73, 264, 385 (1928).

the solution from D and D′ enters header J by means of the tubes H and H′. The solutions pass from the headers to the jets by means of sixteen holes, eight being drilled symmetrically through each plate. In the cross section view, two of the holes are indicated as K. All of the holes in the back plate are designated in a similar manner in the view of the face of the rear plate. The solution from C and C′ passes through the header I and the holes K into eight alternate jets. These jets are 1 mm. deep and at the entrance to the mixing chamber they are approximately 1 mm. wide. The mixing chamber L is 12 mm. in diameter and 1 mm. deep and approximately of 0.1 cc. volume. The solutions enter it at high velocity and in a direction tangent to the outer edge. The

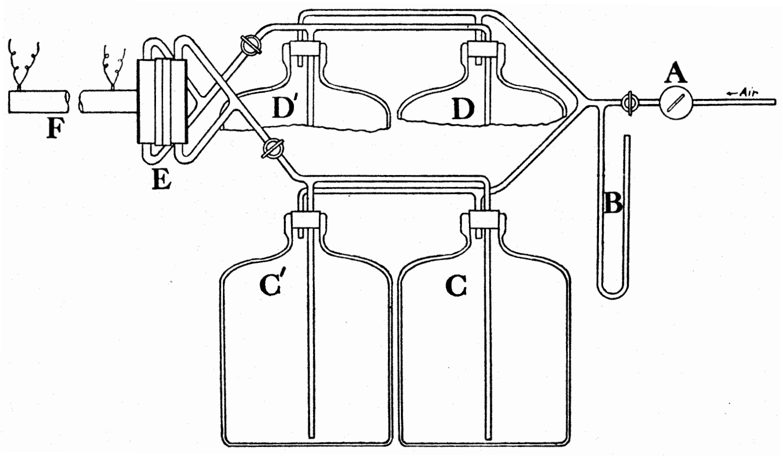
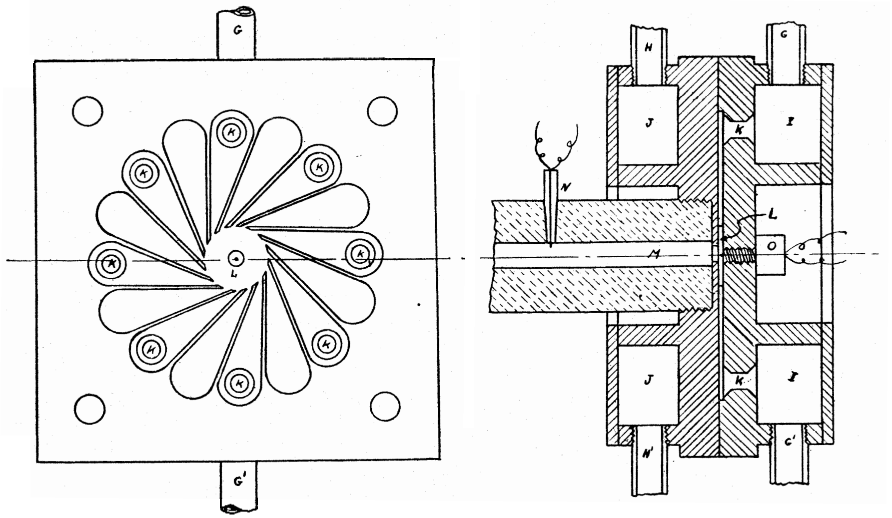


Fig. 1.—Schematic diagram of apparatus.



View of face—rear plate.

Cross section of mixing device and reaction tube.

Fig. 2.

swirling motion produced results in rapid mixing. The mixed solutions pass into the reaction tube M which is a hard rubber tube of 6.35 mm. bore. Thermocouple junctions, mounted on hard rubber pegs as N, are placed at intervals along the reaction tube. The first junction, which is not shown in the sketch, is 1 mm. from the mixing chamber. The cold or reference junction O is mounted on a hard rubber screw, the junction being in the center of the mixing chamber.

Flow of Solutions.—It is essential that the rate of flow of the mixed solution through the reaction tube be as nearly constant as possible while a set of readings is being taken and also that this solution be composed of equal volumes of the reacting solutions. The rate of flow through the apparatus is approximately proportional to the square root of the pressure applied, so small changes in pressure do not greatly influence the rate of flow. This is especially true when high pressures are applied. The pressure could be easily regulated and the fluctuations during an entire run were less than 1 mm. of mercury. Bottles of large cross section containing 36 liters of each solution were used in order that there might be little change in the level of the solutions during a run and consequently little change in the effective pressure applied to them. The variations in flow were less than 1% during a half hour period.

In each system the solution containers and the connections to the mixing apparatus were as nearly identical as possible in order that the liquid levels might remain the same in all four bottles and that each system might offer the same resistance to the flow of the liquid. Several methods were used to determine the ratios of rates of flow in the two systems under various conditions. The stopcock on one side was closed and the rate of flow through the other system was determined for various pressures. This side was then closed off and the rate of flow through the other system was determined. The rates of flow for each side for a given pressure checked within the limit of accuracy for this measurement, ±0.5%.

One set of bottles was filled with 0.05 N hydrochloric acid and the other set with sodium hydroxide of equal strength. Various pressures were applied to the bottles and the stopcocks were adjusted for each pressure so that the greatest possible temperature rise between the mixing chamber and a given junction was obtained. This would occur when the reacting solutions were present in equal concentration. This condition always existed when the stopcocks were wide open. Under these conditions the solution leaving the reaction tube was neutral to litmus paper.

For any set of readings the variation in rate of flow was not greater than 1% and the variation in concentration of the reacting solution was less than 0.5%.

Thermocouples.—Copper–constantan thermocouples of No. 30 wire were used. A Leeds and Northrup type HS galvanometer could be connected between the cold or reference junction and any of the hot junctions by means of a series of switches. The galvanometer was connected in the copper side of the thermocouple circuit and all contacts were of copper in order to eliminate thermal effects. The galvanometer setting, the switchboard and the reaction apparatus were shielded to provide protection from stray currents.

The galvanometer was mounted on the wall above the apparatus and 1.5 meters from the lamp and scale used with it. The temperature difference between two junctions was obtained directly from the deflection. The period of the galvanometer was 7.5 seconds and by having the external resistance in the circuit approximately that of the critical damping resistance of the instrument, a reading could be taken in ten to fifteen seconds.

Each thermocouple junction of the set used gave the same deflection within 0.1% for a given temperature gradient between it and the cold junction. Before installing the junctions in the apparatus they were connected to the switchboard and the galvanometer was calibrated over the desired temperature range. This was accomplished by attaching the cold or reference junction to the bulb of one Beckmann thermometer and the remaining junctions to the bulb of a second Beckmann. The thermometers were then placed in Dewar flasks filled with water at room temperature. The water in the first flask was gradually cooled so that after several hours it was 0.5" colder than the water in the other flask. Readings were taken at short intervals of the temperature difference between the contents of the two flasks and the corresponding deflection given by the galvanometer. The temperature-deflection relationship was linear, a temperature differential of 0.1" giving a deflection of 7.225 cm.

The thermocouple junctions were coated with bakelite varnish and mounted on conical pegs, the wires being fitted into small grooves on opposite sides of the pegs. The remaining space in the grooves was filled with varnish. The peg was fitted into a hole in the reaction tube at a measured distance from the mixing chamber. It was found that when there was an appreciable temperature differential between the reaction solution in the reaction tube and the thermocouple wires going from the tube, heat was conducted to or from the junction and the true temperature differential between this point and the mixing chamber was not recorded. Much of this error was eliminated by winding 20 to 25 cm. of the copper and constantan wires, adjacent to the junction, around the reaction tube and then giving the whole apparatus a heavy coating of paraffin.

The first three junctions (not shown in Fig. 2) were placed so close together and so close to the end of the tube that it was not possible to mount them on pegs. Two narrow slits were cut in the tube and the wires were run through these slits. The junctions were held in place by means of bakelite varnish.

Nine junctions were placed in the reaction tube, the distances from the front end of the tube being 1, 4, 10, 20, 50, 100, 250, 500 and 1000 mm. When the rate of flow of the reacting solutions through the tube was 50 cm. per second, the first reading was taken 0.004 second after mixing and the last reading, 2.00 seconds after mixing. When the rate of flow was 100 cm. per second, the corresponding times were just half these values.

The reference junction O was mounted on a hard rubber peg which screwed into the back plate of the mixing apparatus in such a manner that the junction was in the middle of the mixing chamber. Junctions were also placed in the tubes leading to the mixing apparatus in order to determine the temperature difference between the solutions entering the apparatus.

Temperature Control.—The four 18-liter bottles containing the solutions were kept in a large water thermostat regulated to 25 ± 0.005°. The solutions were placed in the thermostat at least twenty-four hours prior to a run to allow ample time for them to reach the temperature of the bath. The reaction apparatus was mounted in a wooden tank and water from the thermostat was circulated through it. The rate of circulation was rapid and the tank capacity small in comparison with that of the thermostat. The temperature of the tank was maintained within 0.005" of that in the thermostat. Precise temperature control was found to be essential in securing concordant data.

3. Procedure

Air was applied to the solution bottles and regulated to the desired pressure. The stopcocks were then opened and the solutions allowed to flow through the apparatus. The rate of flow was measured by determining the time required for a given volume of solution to flow from-the end of the reaction tube. If the rate of flow was not that desired, the pressure was regulated to give the desired flow. Thermal equilibrium was not reached immediately, so the first temperature readings were taken several minutes after the flow had been regulated. The data recorded for each set of readings consisted of the temperature difference between the two solutions as they entered the mixing apparatus, the temperature differences between the mixing chamber and each of the nine junctions, the air pressure and the rate of flow before and after taking the temperature readings. The first set of temperature readings was usually quite close to equilibrium and this condition was attained within ten minutes. Four or five sets of readings were taken at three- to five-minute intervals after the system had reached equilibrium.

4. Reagents

Analyzed chemicals obtained from J. T. Baker Chemical Co. and from Eimer and Amend were used without further purification. The solutions were made up and standardized against standard solutions. If the concentrations were not within 0.3% of that desired, they were adjusted within that limit. The sodium hydroxide contained approximately 0.1% of sodium carbonate and the solutions were standardized against hydrochloric acid solution. The sodium dichromate solutions were standardized against sodium thiosulfate solution.

5. Acid–Base Reactions—Proof of Mixing

The reaction between sodium hydroxide and hydrochloric acid, which was studied by Hartridge and Roughton, was used to check the effectiveness of mixing with this apparatus. The first temperature reading was taken 0.002 second after mixing, and since this reaction is complete in less than 0.001 second, the temperature rise equivalent to the heat of reaction for the complete reaction should be obtained at the first junction, if the mixing is complete at that point. Solutions of hydrochloric acid and sodium hydroxide of 0.05 normal concentration were run through the apparatus, the rate of flow through the reaction tube being 100 cm. per second. The corrected temperature differences between the mixing chamber and each of the junctions in the reaction tube were within 0.004' of 0.340''. Calorimetric data require that this value should be 0.342'.

These results prove that mixing is complete before the first junction in the reaction tube is reached and also that the entire reaction takes place between the cold junction and the first hot junction. It is evident that mixing does not take place until the reacting solutions reach the center of the mixing chamber.

Saal has studied various acid–base reactions, apparently using a strong acid with a weak base or a strong base with a weak acid. He concluded that these reactions are all complete to within 1% in less than 0.004 second. The reaction between a weak acid and a weak base has not been reported, so the reaction between acetic acid and ammonium hydroxide was observed. Using 0.05 normal solutions, it was found that the reaction was 95% complete in 0.002 second and equilibrium was reached in less than 0.01 second. The temperature rise for this reaction was 0.192'. These results indicate that the strength of the acid and base do have an effect on the velocity of neutralization. We intend to study this question in more detail in a later publication using an improved instrument.

An attempt was made to use still weaker acids and bases but the results were not satisfactory. The heat of neutralization is to a large extent offset by the increased heats of ionization, so that unless solutions of high concentration are used, the temperature rise due to the heat of reaction is not much greater than the experimental errors.

6. Neutralization of Sodium Dichromate by Sodium Hydroxide

This reaction is usually written as follows

$$Na_2Cr_2O_7 + 2NaOH \longrightarrow 2Na_2CrO_4 + H_2O$$

It was found to be well suited for study with this apparatus as it reaches equilibrium in one to two seconds and the heat evolved was comparable to that evolved on the neutralization of a moderately strong acid. Sodium dichromate solutions of 0.02, 0.04 and 0.06 molar concentration were neutralized by sodium hydroxide solutions of equivalent concentrations. The results obtained are given in Table I and are represented graphically in Fig. 3, in which the temperature rise between the mixing chamber and a given junction is plotted against the time required for the mixed solution to

TABLE I

ORIGINAL DATA CORRECTED POR WATER EFFECT

Junction no	Time, sec Curve Ia	Temp., °C Curve Ia	Time, sec Curve Ib	Temp, °C. Curve Ib	Junction no.	Time. sec. Curve IIIa	Temp., °C Curve IIIa	Time, sec. Curve IIIb	Temp., °C. Curve IIIb
1	0 004	0 072	0.002	0.071	1	0.004	0.202	0.002	0.212
2	.010	.077	.005	.072	2	.010	.218	.005	.218
3	.022	.084	.011	.082	3	.022	.255	.011	.232
2	.042	.098	.021	.093	4	.042	.305	.021	.264
5	.100	.124	.050	.111	5	.100	.406	.050	.331
6	.200	.138	.100	.130	6	.200	.472	.100	.417
7	.500	.149	.250	.151	7	.500	.529	.250	.479
8	1.000	..	.500	.152	8	1.000	.540	.500	.529
9	2.000	.166	1.000	.169	9	2.000	.554	1.000	.564
	Curve IIa		Curve IIb			Curve IV		Curve V	
1	0.004	0.150	0.002	0.144	1	0.002	0.148	0.002	0.184
2	.010	.156	.005	.148	2	.005	.152	.005	.186
3	.022	.176	.011	.158	3	.011	.161	.011	.199
4	.042	.206	.021	.170	4	.021	.174	.021	.230
5	.100	.269	.050	.220	5	.050	.209	.050	.306
6	.200	.311	.100	.257	6	.100	.266	.100	.355
7	.500	.315	.250	.291	7	.250	.291	.250	.357
8	1.000	.334	.500	.317	8	.500	.332	.500	.360
9	2.000	.355	1.000	.343	9	1.000	.355	1.000	.360

reach the junction. Curves I, II and III represent the above-mentioned reactions. Each curve represents two sets of data, the velocity of flow through the reaction tube being 50 cm. per second in one and 100 cm. per second in the other. The "a" curves represent the lower velocity and the "b" curves the higher. These curves do not start from the origin and when extrapolated to zero time have finite intercepts.

Curve IV represents the neutralization of 0.04 molar sodium dichromate by 0.16 molar sodium hydroxide, twice the OH– concentration required. This curve is so similar to II that to add the additional data to the graph would only make it more difficult to identify the points for curves Ia and Ib. These data prove that the velocity of the reaction is not affected by the OH^- concentration.

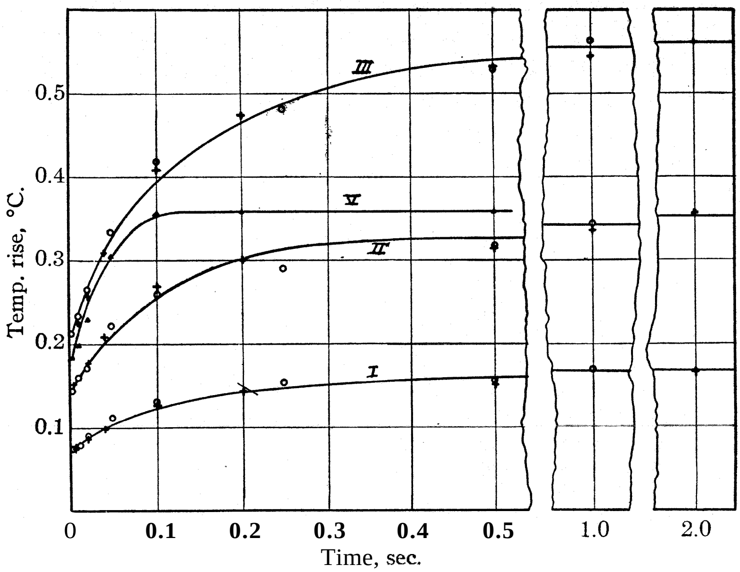


Fig. 3.—Graph of original data.

Curve V represents the partial neutralization of 0.08 molar sodium dichromate by 0.08 molar sodium hydroxide, half the OH– concentration required for the neutralization. This curve is quite different from curve II as it rises much more rapidly until the OH– is used up. These data show that the velocity of the reaction is a function of the concentration of the dichromate ion.

The data for the equilibrium between dichromate and chromate yield an explanation for these curves. Sherrill[6] has investigated the equilibrium between dichromate and hydrochromate by a freezing point method.

$$Cr_2O_7^{=} + H_2O \rightleftharpoons 2HCrO_4^- \qquad K_1 = (HCrO_4^-)^2/(Cr_2O_7^{=})$$

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[6] Sherrill, THIS JOURNAL, 29, 1641 (1907).

The values of K_1 vary from 0.0145 to 0.0196 over a concentration range of 0.01 to 0.05 molar potassium dichromate. The dissociation of the hydrochromate ion was determined from the hydrolysis of ammonium chromate and also from distribution data.

$$HCrO_4^- \rightleftarrows H^+ + CrO_4^= \qquad K_2 = (H^+)(CrO_4^=)/(HCrO_4^-)$$

The values for K_2 are given as 5.2 to 5.9 × 10^{-7} at 18° and 7.4 × 10^{-7} at 25°.

Saal has redetermined the value for K_1 by measuring the amount of OH– required to neutralize rapidly the $HCrO_4^-$ in equilibrium with the $Cr_2O_7^=$. He found the value of K_1 to be 0.019 ± 0.001 for concentrations up to 0.125 molar in potassium dichromate. On the basis of this value of K_1, the concentrations of $Cr_2O_7^=$ and $HCrO_4^-$ present in equilibrium in the sodium dichromate solutions used have been calculated and are given in Cols. 5 and 6 of Table II. For the concentration range used in these experiments, approximately one-third of the chromium is present as the hydrochromate. The sudden rise in the temperature–time curves can be explained on the basis of the very rapid reaction between the $HCrO_4^-$ present and the OH–. This is in agreement with the evidence previously offered that acid–base

TABLE II

ANALYSIS OF EXPERIMENTAL DATA

1 Run no.	2 Concn. of $Na_2Cr_2O_7$ taken, mole/l.	3 Concn. of NaOH, mole/l.	4 Velocity of mixed solns. through R. T., cm./sec.	5 Concn. of $Cr_2O_7^=$, mole/l.	6 Concn. of $HCrO_4$, mole/l.	7 ΔT between M. C. and last junction, °C.	8 ΔT due to heat of diln. of $Na_2Cr_2O_7$, °C.	9 ΔT due to heat of neutn., 7 + 8, °C.
Ia	0.02	0.04	50	0.0124	0.0152	0.166	−0.010	0.176
Ib	.02	.04	100	.0124	.0152	.169	−.010	.179
IIa	.04	.08	50	.0284	.0232	.355	−.019	.374
IIb	.04	.08	100	.0284	.0232	.343	−.019	.362
IIIa	.06	.12	50	.0453	.0294	.554	−.021	.575
IIIb	.06	.12	100	.0453	.0294	.564	−.021	.585
IV	.04	.16	100	.0284	.0232	.355	−.019	.374
V	.08	.08	100	.0627	.0346	.360	..	..

Run no.	10 ΔT, between junctions 1 and 9, °C.	11 ΔT 10 extrapolated to zero time, °C.	12 Theoret. ΔT for the reaction had there been no initial hydration of the $Cr_2O_7^=$, °C.	13 Diff. between actual ΔT and theoret., 9–12, °C.	14 Heat of reaction $Na_2Cr_2O_7 + 2NaOH — 2NaCrO_4 + H_2O$ steps "a" + "b" + "c," cal/mole of $Cr_2O_7^=$	15 Heat of hydration of $Cr_2O_7^=$ in forming $HCrO_4^-$ Cal./mole of $Cr_2O_7^=$
Ia	0.094	0.097	0.156	0.020	+15,600	(−5270)
Ib	.098	.100	.161	.018	+16,100	(−4740)
IIa	.205	.210	.296	.078	+14,800	−13,500
IIb	.199	.201	.283	.079	+14,150	−13,600
IIIa	.352	.363	.489	.095	+16,000	−12,900
IIIb	.352	.362	.479	.106	+16,000	−14,400
IV	.207	.209	.294	.080	+14,700	−13,800
V	.176	.196	.345	..	......	......
					Av., +15,320	**Av.**, −13,640

reactions reach equilibrium in a very few thousandths of a second, even when one of the components has a small dissociation constant.

The mechanism of the reaction between sodium dichromate and sodium hydroxide is postulated to take place in three steps, as follows

$$Cr_2O_7^{=} + H_2O \rightleftharpoons 2HCrO_4^{-} \qquad (a)$$
$$HCrO_4^{-} \rightleftharpoons H^{+} + CrO_4^{=} \qquad (b)$$
$$H^{+} + OH^{-} \longrightarrow H_2O \qquad (c)$$

The steps "b" and "c" take place in the interval of time between the mixing of the solutions and their reaching the first junction in the reaction tube. From analogy with other hydration reactions step "a" must be slow and this reaction is the one whose velocity is measured. The concentration of the water is large in comparison with that of the $Cr_2O_7^{=}$ so it would be expected that the rate of hydration would be pseudo-monomolecular and of the first order in respect to $Cr_2O_7^{=}$. This is in agreement with the data already presented.

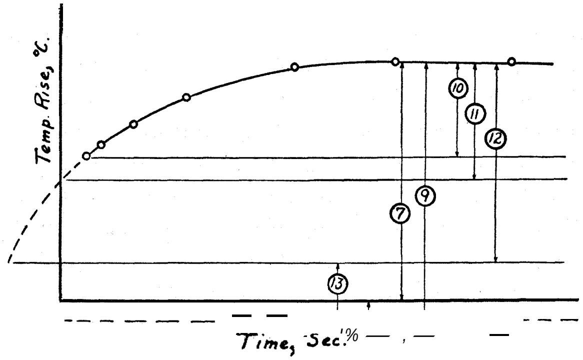

Fig. 4.—Diagrammatic representation of temperatures.

The heat effects of the various steps may be obtained from an analysis of the experimental data give in Table II and a graphic representation of the various items given in Fig. 4. Col. 1 in Table II gives the number of the run, Cols. 2 and 3 the concentrations of the reacting solutions, and Col. 4 the velocity of the mixed solutions through the reaction tube. It will be noted that the "b" curves are duplicates of the "a" curves except that the velocity through the reaction tube is 100 cm. per second instead of 50 cm. per second. Cols. 5 and 6 represent the concentrations of $Cr_2O_7^{=}$ and $HCrO_4^{-}$ present in the sodium dichromate solutions. Column 7 gives the temperature rise between the mixing chamber and the last junction in the reaction tube. This item and the succeeding ones are represented in Fig. 4. A small correction has been applied to these values to correct for the temperature change due to the friction of water passing through the apparatus. To obtain the temperature rise due to the three steps "a," "b" and "c," the heats of dilution of the reacting solutions must be taken into account. The heat of dilution of sodium hydroxide is quite small and may be neglected. This is not the case with sodium dichromate. The temperature change due to the dilution of the various concentrations of sodium dichromate with equal volumes of water has been determined experimentally by means of the reaction velocity apparatus and these values are given in Col. 8. This correction must be applied to the values given in Col. 7 in order to obtain the true temperature rise due to the steps "a," "b" and "c." This latter value is given in Col. 9.

The temperature rise between junctions one and nine is given in Col. 10. The curves given in Fig. 3 may be extrapolated to zero time. The temperature difference between this intersection with the zero ordinate and the ninth junction is given in Col. 11. This temperature rise is due to the hydration of that concentration of $Cr_2O_7^=$ initially present in the aqueous solution (Col. 5) and the subsequent neutralization of the $HCrO_4^-$ formed. Prom this temperature rise and the initial concentration of $Cr_2O_7^=$, the theoretical temperature rise obtainable if there were no initial hydration can be computed. This value is given in Col. 12. It is the temperature rise due to the reactions "a" + "b" + "c," and the heat effect per mole of $Cr_2O_7^=$ can be obtained from this value and the concentration of the sodium dichromate solution. The values for the sum of the heat effects of these three steps are given in Col. 14, the average value being +15,320 ± 675 calories per mole of $Cr_2O_7^=$. In making the calculations for the heat effects no allowance has been made for the reduced specific heat or the increased specific gravity of the solutions due to the presence of the salt. These effects tend to offset each other so that the results given are probably about 1% high for the most concentrated solutions. Sufficient data are not available for the calculation of such a correction and it is of the same order of magnitude as the experimental error.

The theoretical value of the temperature rise for these three steps (Col. 12) is considerably less than the gross temperature rise experimentally determined (Col. 9). The difference, Col. 13, is a measure of the heat of hydration of the $Cr_2O_7^=$ or step "a." The heat of hydration is then calculated from the concentration of $Cr_2O_7^=$ initially hydrated and the temperature difference given in Col. 13. The calculated values for this heat of hydration are given in Col. 15. The values for runs Ia and Ib are not in agreement with the remaining values and they have been omitted in determining the average value of −13,640 calories per mole of $Cr_2O_7^=$. The calculations of the heat of hydration are dependent upon a very small temperature increment, 0.020 and 0.018° for runs Ia and Ib, so a large experimental error is not required to alter these values greatly.

The heat effects for steps "a" + "b" + "c" and for step "a" have been computed from the experimental data. The value for step "c" has been well established as +13,700 calories per mole. The value for "b," the heat of dissociation of the $HCrO_4^-$ into H^+ and $CrO_4^=$, then becomes +780 calories per mole.

The neutralization of sodium dichromate has been assumed to be a pseudo-monomolecular reaction. If this assumption is correct, a straight line should be obtained when log $a/(a - x)$ is plotted against time where a is the concentration of dichromate originally present and x is the concentration which has been neutralized at the time t. In this case the temperature change was used as a measure of a and x, the value of a being given in Col. 12. The data are represented in Fig. 5. The dichromate initially hydrated varied from 24.5 to **38%** so the points do not give a single line but three lines. The intersection of these lines with the abscissa gives the correction to be applied for the construction of theoretical curves based on an

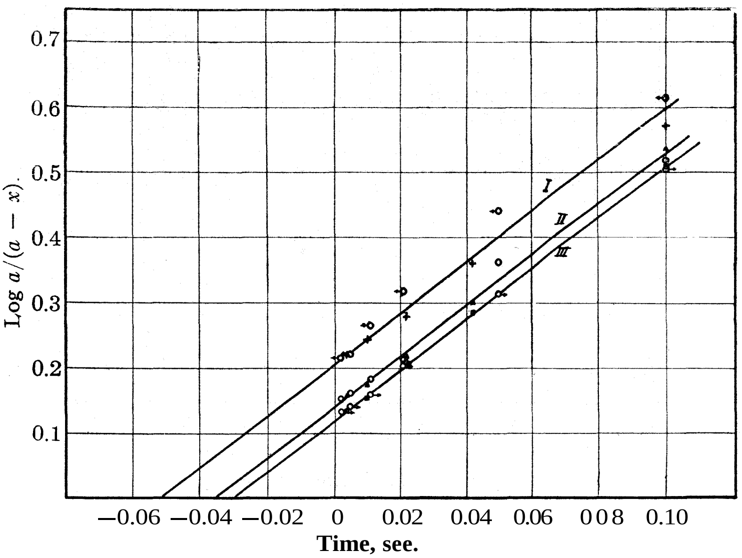

Fig. 5.

TABLE III

MONOMOLECULAR CONSTANTS FOR THE NEUTRALIZATION OF $Cr_2O_7^=$ BY OH^- IN $MIN.^{-1}$

$k = 1/t \ln a/(a-x)$

Junction no.	Ia	Ib	IIa	Curve no IIb	IIIa	IIIb	IV
1	524	534	549	553	529	562	556
2	495	516	517	546	522	542	543
3	507	567	520	541	535	520	532
4	518	602	528	518	539	539	436
5	498	576	545	582	538	535	490
6		553	486	526	459	542	527
Average	**508**	558	524	544	518	540	514

Average of **all values,** 529.4.

initial condition of no hydration of the dichromate ion. The constants for the reaction can be calculated from the corrected times and they are given in Table III. Values corresponding to the first six junctions are given, the sixth junction representing the reaction about 75% complete. Beyond this point, a small error in the value of x has a very pronounced effect on the values $\ln (a/a - x)$ and the results are not reliable. The average value for the constants for the seven experiments is 529.4 min.^{-1}.

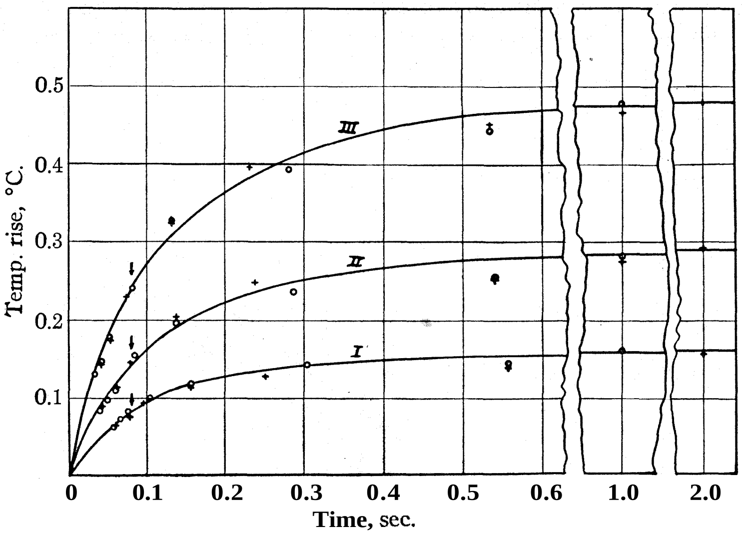

Fig. 6.—Theoretical curves.

Theoretical curves for the neutralization of $Cr_2O_7^{=}$ by OH– can be plotted by applying the time corrections obtained in Fig. 5 and the values for the neutralization had there been no initial hydration given in Col. 12. These curves are given in Fig. 6. The half time of 0.0785 second is obtained from the velocity constant.

7. Discussion of Results

Saal has studied the neutralization of potassium dichromate by sodium hydroxide by conductivity methods and on the basis of a very limited amount of data has concluded that the reaction is bimolecular. He considers the mechanism to be as follows

$$HCrO_4^- + OH^- \rightarrow CrO_4^= + H_2O$$
$$Cr_2O_7^= + OH^- \rightarrow CrO_4^= + HCrO_4^-$$

If this mechanism were correct, the reaction would probably be bimolecular but the rate of reaction would depend on the concentration of OH– present. It has been shown that the concentration of OH– has no effect on the rate of reaction. Saal's data are difficult to interpret and it is not possible to recalculate them on the basis of the reaction being monomolecular.

Note of *May* 30, 1930.—Since this paper was submitted for publication, two recent papers by Roughton [Proc. *Roy. Soc.* (London), **A126**, 439, 470 (1930)] have come to our attention, in which the author has published the details of his thermocouple method of following chemical reactions to which he referred briefly in Ref. 3c. He gives an exhaustive analysis of the sources of error involved. Although Roughton's procedure for thermal control differs considerably from ours, he achieves a precision of 0.001° in the heats of neutralization. In the second paper he has studied some reactions of acids, bases and proteins in which the heats of reaction rather than the evaluation of the rate constants were of primary interest.

Acknowledgment.—We wish to express our indebtedness to Dr. J. W. Roughton for advice in the early stages of the investigation and to Mr. L. J. Dornhofer, Chief Mechanician of the Laboratories, for the care which he exercised in constructing the Mixing Chamber.

Summary

1. An apparatus has been described for the study of rapid reactions, the progress of the reaction being followed by means of the temperature rise due to the heat of reaction evolved. The flowing stream method of Hartridge and Roughton has been employed, the reacting solutions being rapidly and completely mixed in a small mixing chamber and the resulting solution passed through a reaction tube at uniform velocity where the progress of the reaction is observed. The temperature rise between the point of mixing and any given point in the reaction tube was measured by thermocouples placed at measured intervals along the reaction tube, corresponding to time intervals which may be computed from the rate of flow.

2. The neutralization of $Na_2Cr_2O_7$ by sodium hydroxide has been studied at 25° with this apparatus. It has been shown that the following mechanism

$$\begin{array}{lll} \text{(a)} & Cr_2O_7^{=} + H_2O \rightleftharpoons 2HCrO_4^{-} & \text{(slow)} \\ \text{(b)} & HCrO_4^{-} \rightleftharpoons H^{+} + CrO_4^{=} & \text{(fast)} \\ \text{(c)} & H^{+} + OH^{-} \longrightarrow H_2O & \text{(fast)} \end{array}$$

will account for the peculiarities of the reaction. Reaction "a" is pseudo-monomolecular with a half time of 0.0785 second and $k = 529$ reciprocal minutes. The heat of the gross reaction is $+15,320$ calories per mole of dichromate ion. The streaming method permits the determination of the heats of reaction involved in steps "a" and "b" which are not accessible by the usual methods. $q_a = -13,640$ calories per mole of $Cr_2O_7^{=}$ and $q_b = +780$ calories per mole of $HCrO_4^{-}$.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

DEFORMATION OF ELECTRON SHELLS. I. ABSORPTION SPECTRUM, MOLECULAR VOLUME AND REFRACTION OF NEODYMIUM PERCHLORATE

BY P. W. SELWOOD

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The object of this work was to investigate the relations existing between the absorption spectrum and other properties of certain rare earth salts. As pointed out by Foex[1] in a recent article on the "Different Magnetic States of an Ion:" "If each magnetic state corresponds to a special structure of the outer electron layer, it may be expected that all of the properties of the ion which depend on that outer layer will change with the changes that occur in this layer. For example, the refraction of the ion, the absorption bands, the magnetic rotation, polarization, etc., would change when the magnetic state changes. These changes and co-relations have not as yet been investigated."

During the course of work on the absorption spectra of the rare earths by Quill, Selwood and Hopkins,[2] it was observed that the spectrum of neodymium and other rare earth salts in solution could be altered by the addition of excess of a common ion or merely by changing the concentration. In general, the absorption bands of neodymium salts and, to some extent, those of other rare earths investigated were shifted toward the red end of the spectrum by increased concentration.

Regarding the possible mechanism of these absorption band shifts, the authors have this to say, "It is known that even in the case of strong electrolytes the oppositely charged ions in solution may approach close enough to one another to cause distortion of the outer electron shells. It is probable that the distortion may be communicated in part, as small energy changes, to the electrons composing the inner sub-group which is thought to be the seat of the spectrum bands in the visible region. Recent observations by Ephraim and Bloch on the ammonia complexes of praseodymium chloride have been successfully explained by them on the basis of their theory of the deformation of the inner electron shell."

The relation between molecular volume and absorption spectrum has received considerable attention from Ephraim and co-workers.[3] Briefly, the object of their investigations has been to determine whether the deformation of the outer electron shell resulting from chemical union is transmitted to the inner shells. The rare earths are ideal for such an investigation. Ephraim maintains that a chemical union which is attended by a

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[1] Foex, Trans. *Am. Electrochem. Soc.*, 55, 97 (1929).

[2] Quill, Selwood and Hopkins, THIS JOURNAL, 50, 2929 (1928).

[3] Ephraim and Bloch, *Ber.*, **59B**, 2629 (1926); *ibid.*, **61B**, 65, 72, 80 (1928); Ephraim and Ray, *ibid.*, **62B**, 1509, 1520, 1639 (1929).

diminution of molecular volume results in compression of the electron shells, bringing about a shorter period of vibration and a corresponding shift to the violet in the absorption bands. No matter what the theoretical interpretation of Ephraim's results, there can be no question that the extension of his observations to solutions of rare earth salts should provide valuable confirmatory evidence for the deductions which may be drawn from absorption and refraction.

A basis for the work on molecular refraction has been established by Fajans and co-workers.[4] Taking as his primary postulate that the familiar Lorentz–Lorenz expression $R = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$ is strictly additive unless changes occur in the electron shell, he considers deviations of R as being measures of such changes. Fajans maintains that the close proximity of an anion to a cation will result in an increase in the refraction of the latter proportional to the charge on the anion and to the polarizability of the cation. Conversely, the refraction of an anion is diminished by the approach of a cation.

From the standpoint of the classical Clausius–Mosotti theory of dielectrics, a shift of the absorption bands toward the red should be attended with an increase of molecular refraction. To be sure, absorption bands have to do with only a few electrons in the cation, while refraction has to do with all the electrons in cation, anion and solvent molecule as well; but as pointed out by Fajans, some means are available for the estimation of these various effects.

Experimental

Preparation of Solutions.—The measurements described here were carried out on solutions of neodymium perchlorate. When the work was started neodymia was the only rare earth available in sufficient quantity (about 1000 g.) for the purpose. The neodymium had been prepared by fractional crystallization of the double magnesium nitrate by the writer and others during the past two years. The rich blue color of the oxide and the absence of absorption spectrum bands of other rare earths were taken as evidences of purity.

Perchlorate was chosen because, as has been pointed out by several workers, the refraction of the perchlorate ion is only slightly influenced by concentration or other external influence.[5]

More than sufficient neodymium oxide to prepare 100 cc. each of seven

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[4] Fajans, *Naturwissenschaften*, 11, 165 (1923); *Trans. Faraday Soc.*, 23, 357 (1927); Fajans and Joos, *Z. Physik*, 23, 1 (1924); Fajans, *Z. physik. Chem.*, 130, 724 (1927); Fajans, Kohner and Geffcken, *Z. Elektrochem.*, 34, 1 (1928); Fajans, *ibid.*, 34, 1 (1929); *Z. Physik*, 50, 531 (1928); *Z. physik. Chem.*, A137, 361 (1928); *Z. Krist.*, 66, 321 (1928).

[5] Mazzucchelli and Vercillo, *Gazz. chim ital*, 55, 498 (1925).

solutions from about 2 to 7 N in neodymium perchlorate was treated with insufficient perchloric acid to effect complete solution. The mixture was subjected to prolonged boiling and was then filtered. The clear filtrate was analyzed for neodymium content and appropriate quantities were removed and evaporated down to the desired concentration. The solutions finally obtained were clear and neutral to litmus.

Analytical Procedure.—Preliminary tests indicated two methods which might be used for the analysis of the solutions. These were, first, precipitation of the neodymium as oxalate with standard oxalic acid, filtering, and back-titration of the excess oxalic acid in the filtrate with standard permanganate; and, second, ignition of the oxalate to oxide which may be weighed directly. Neither of these methods was very satisfactory, and they do not compare in accuracy with the other measurements necessary in the determination of molecular refraction. Both methods were conveniently run on the same weighed sample of solution. The possible oxidation of oxalic acid by the liberated perchloric acid was investigated by standardizing the former against permanganate first in sulfuric acid solution and then in perchloric acid. No difference could be detected, so it was assumed that dilute perchloric acid had no effect on oxalic acid.

The weighed samples of the neodymium perchlorate solutions were acidified with a few drops of dilute sulfuric acid, diluted with water and heated just to boiling. Standard oxalic acid solution to the extent of about one and one-quarter times the amount required to precipitate all the neodymium was added and the mixture was allowed to cool, and if convenient to stand overnight. The mixture was then filtered, the precipitate thoroughly washed, the filtrate was heated to boiling and quickly titrated with standard potassium permanganate solution after the addition of 5 cc. of 6 N sulfuric acid. The neodymium oxalate was dried and ignited in porcelain to constant weight over the full heat of a Méker burner. This required several hours. The oxide was allowed to cool in a carbon dioxide-free desiccator and was weighed. No tendency to increase in weight was observed.

The results obtained by the oxide method were, in general, 1% higher than those by the permanganate method. Good checks were secured by both methods although the oxide checks were better. When the oxide results were plotted against refractive index, the curve obtained was much smoother than when the permanganate results were used. The neodymium oxide when dissolved in nitric acid gave no test for chloride, thus eliminating the possibility of oxalo-perchlorate formation. In view of these facts, and the more direct procedure involved in the oxide method, the results obtained by that method were used exclusively in the calculation of refractions and volumes. The compositions of the solutions given are believed to be accurate to 0.2%. The irregularities in the refraction and volume curves are believed by the writer to be attributable to the unavoidably high probable error in the analytical work. A single determination by weighing the oxalate in a sintered glass crucible after drying at 125° gave an excellent check with the oxide determination on the assumption that the oxalate was associated with one molecule of water. The reliability of this method is, however, said to be open to serious question.[6]

Densimetry.—The densities of the solutions were determined pycnometrically and

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[6] Little (Friend), "Textbook of Inorganic Chemistry," Vol. IV, 1921.

by Archimedes' principle. The temperatures were read to 0.1° on a mercury thermometer calibrated against a Bureau of Standards thermometer. In the case of the most concentrated solution which had the largest temperature coefficient, 0.1" was approximately equivalent to 0.1 mg. on the balance pan, so that nothing could have been gained by more sensitive temperature control. The density of each solution was determined at at least four different temperatures. The densities were plotted against temperature, and the value at the temperature at which the refractive indices were determined was found by interpolation. The maximum probable error is believed to be about 0.02%. The values obtained by the two methods agree within this amount.

Refractometry.—The refractive indices of the solutions were measured on an Eykmann refractometer. The large number of intense absorption bands in the spectrum of neodymium salts rendered it possible that anomalous dispersion would completely mask the small deviations it was hoped to detect. It became necessary, therefore, to plot the refractive index of a concentrated solution over a range of wave lengths in the neighborhood of the yellow and red portions of the spectrum. Figure 1 shows the refractive index of a nearly saturated (about 10 N) solution of neodymium nitrate from 4554 to 6708 Å. Most of the wave lengths were obtained from salts of barium placed in the positive crater of a carbon arc. The very slight deviation of the hydrogen C line is attributed to a small change in the position of the source when the change was made from an arc to a Geissler tube. Otherwise the refractive indices lie on a smooth curve, and any anomalous dispersion, if present, must be within the observational error. These results are in accord with those of Elias,[7] who found very slight anomalous dispersion in the region of the intense neodymium band in the yellow.

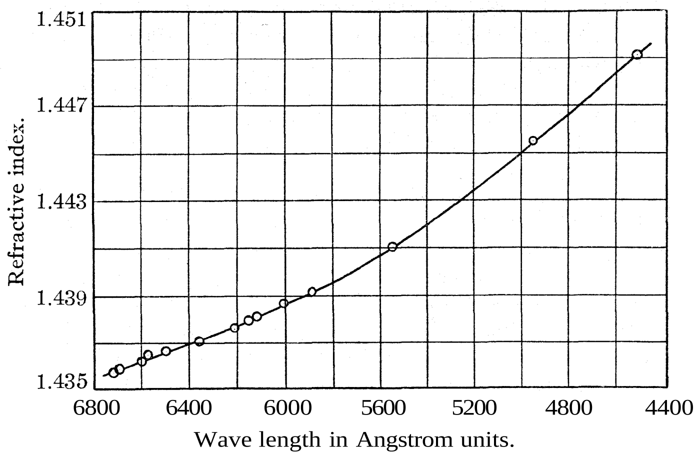

Fig. 1.—Dispersion of saturated $Nd(NO_3)_3$ solution.

The refractive indices used in estimating molecular refraction were all found for the hydrogen C line (6563 Å.) which is in a region comparatively free from absorption. The measurements were made at room temperature, which was read to 0.1" on a calibrated thermometer suspended directly in the solution. The refractive indices were corrected to vacuum and are believed to be accurate to 0.003%.

Absorption Spectrum.—Although some investigators have stated that solutions of neodymium salts obey Beer's laws throughout considerable ranges of concentration, it has been shown elsewhere that this is not true. The present paper indicates that

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[7] Elias, Ber. *Physik.* Ges., 955 (1910).

absorption band shifts may be found in even the moderate concentrations (about 7 N) obtainable with neodymium perchlorate.

For the purpose of this work the absorption spectrum of the highest concentration of neodymium perchlorate prepared (6.63 N) through a 3-mm. layer was compared with that of a 0.1989 N solution through the equivalent thickness of 100 mm. In the case of the more dilute solution it was believed that the rare earth ions were completely surrounded by water molecules, or their electron shells, at any rate, were shielded from the influence which produces absorption band shifts. Unpublished work by the writer indicates that Beer's law is rigorously obeyed by solutions of rare earth salts from about 0.2 *N* down. The spectra were registered photographically on a Hilger E 1 quartz prism spectrograph, using a quartz system throughout. The light source was a tungsten ribbon incandescent lamp which gave a steady light and a fairly uniform continuous spectrum in the region involved. The curves shown in Fig. 4 are tracings of the curves obtained from the photographic plate on a recording microphotometer.

The longer absorption cell was a glass tube fitted with quartz windows. In order to reduce the relatively large error possible in measurements of 10 mm. or less, the shorter cell was made of brass, gold-plated and ground to the proper dimensions. It was also fitted with quartz windows.

The most serious difficulties in connection with the spectrographic work were the location of satisfactory reference points from which to compare the two microphotometric curves, and the establishment of the highest possible degree of uniformity in exposure and development of the plate.

The first difficulty was readily solved by placing a solution of europium nitrate in the optical train before the slit of the spectrograph. The sharp, intense absorption lines of this element at about 4650 and 5250 Å. are indicated in Fig. 4.

The method used by Jones[8] for procuring uniformity of exposure through long and short absorption cells was one of trial and error where the time of exposure was varied until approximately equivalent blackening of the photographic plate was obtained. In view of the very slight deviations expected in this work, such a method did not seem satisfactory to the writer. Resort was, therefore, made to the following arrangement. Both the long and short cells were left in place throughout both exposures. In the first case the longer cell was filled with the more dilute solution and the shorter cell with water and the plate was then exposed for five minutes. In the second case the longer cell was filled with water and the shorter one with the more concentrated solution. The exposure was again for five minutes. In this way the only possibility of error was in variations in intensity of the light source. The intensity was controlled as closely as possible, and plates wherein it had appeared to vary were rejected. In order further to insure uniformity, the two spectra were taken as near together as possible on the same plate, and the usual precautions were taken in developing and fixing.

Results

The apparent molecular volume of neodymium perchlorate in solution calculated from the simple mixture law is shown in Pig. 2. The values given are the averages of several determinations at 29.5°, and they show about a 14% increase with increasing concentration. Owing, however, to the fact that no account has been taken of the possibility of change in the specific volume of the solvent, the writer does not care to attach much importance to these results other than in a qualitative sense. As such

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[8] Jones, "Absorption Spectra of Solutions," Carnegie Institute of Washington publications, No. 130, No. 160.

they suggest an agreement with Ephraim's theory which requires an increase in molecular volume to be associated with a decrease of characteristic spectral frequency.

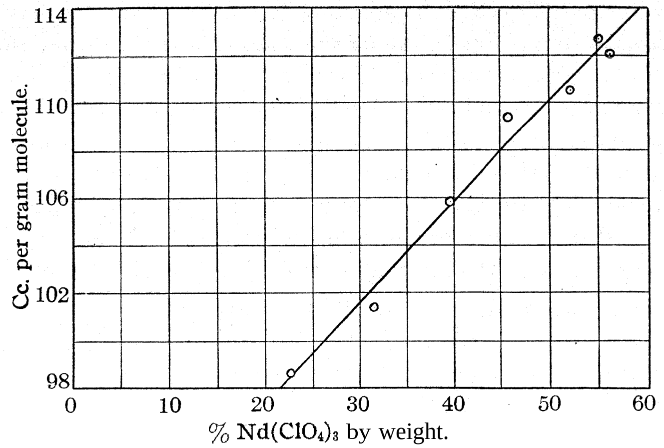


Fig. 2.—Apparent molecular volume of neodymium perchlorate in aqueous solution.

The values for the molecular refraction of neodymium perchlorate are indicated in Fig. **3.** These were calculated from the refractive indices

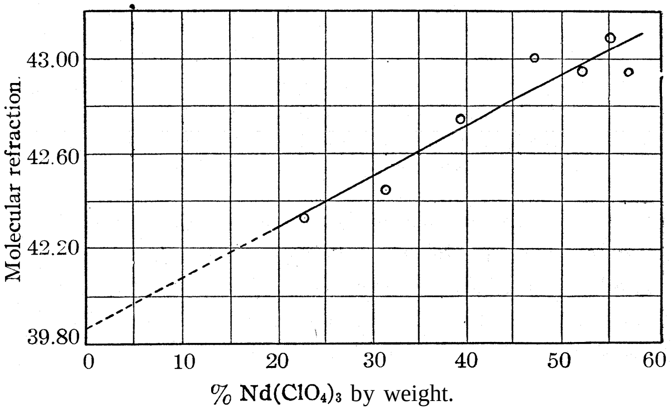
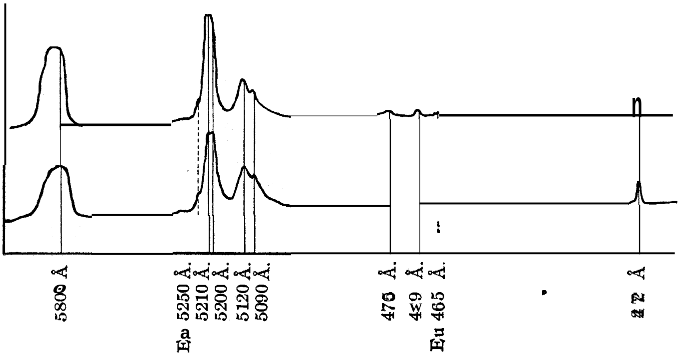


Fig. 3.—Molecular refraction of neodymium perchlorate in aqueous solution.

corrected to vacuum, the absolute densities and the percentage composition by weight, by means of the simple mixture law

$$R = \frac{100\text{ M}}{P}\left[\left\{\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}\right\} - \left\{\frac{n_0^2-1}{n_0^2+2}\cdot\frac{1}{d_0}\right\}\left(\frac{100-P}{100}\right)\right]$$

where R is molecular refraction, M is molecular weight of $Nd(ClO_4)_3$, P is % of $Nd(ClO_4)_3$ by weight, *n* is refractive index of the solution, d is density of the solution, and n_0 and d_0 are the corresponding quantities for water. The molecular refraction shows about a 2% increase from the extrapolated value at infinite dilution to about 7 N. The experimental values given are believed to be accurate to 0.3%, which is about the maximum deviation of any single value from a smooth curve drawn through the points. Each value is the mean of several found for slightly different temperatures between 25 and 30°. Part of the increase in refraction may be ascribed to polarization of the solvent molecule. As such polarization is roughly proportional to the charge on the polarizing ion and inversely to its radius, the effect in this case may be expected to be somewhat less than that estimated by Fajans for the case of aluminum sulfate. In any event, it can scarcely be more than a small part of the observed deviation.



Upper curve, 6.63 N $Nd(ClO_4)_3$ through 3 mm. layer; lower curve, 0.1989 N $Nd(ClO_4)_3$ through 100 mm. layer.

Fig. 4 —Microphotometric curves of the absorption spectrum of neodymium perchlorate.

Increasing concentration brings about quite noticeable changes in the relative intensities of the different absorption bands of neodymium perchlorate. Such changes are apparent from Fig. 4 but the shifts in position at the highest concentration reached are scarcely to be distinguished except under a microscope. There is no question, however, that a shift of most of the bands toward the red has occurred. Figure 5 is an enlarged reproduction of the sharp band at 4272 Å. It will be seen that increased concentration has brought about a shift of approximately 1 Å. toward the red. The shifts of other bands whose positions are less readily measured are of about the same magnitude and in the same direction.

The classical dispersion formula[9] gives for the square of the refractive index

$$n^2 = 1 + \Sigma \frac{N_i e^2 Z_i}{\pi m_i (\nu_{oi}^2 - \nu^2)}$$

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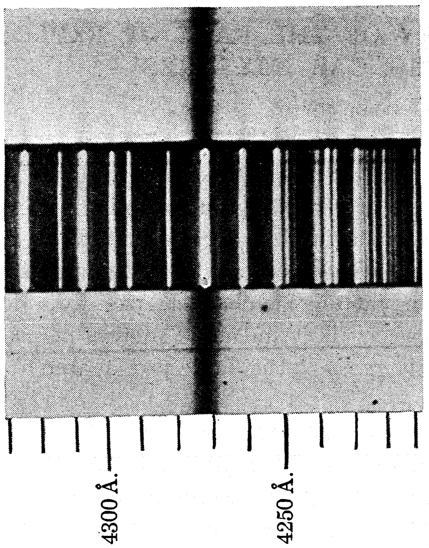
[9] Haas, "Atomic Theory," D. Van Nostrand Co., New York, p. 199.

"In this equation different kinds of electrical charges are assumed to exist and they are distinguished by the subscript i; Z_ie is the quantity of electricity in such a charge, m_i its mass, ν_0 the frequency of its characteristic oscillation and N_i the number of these charges in unit volume." This equation shows that a decrease in characteristic frequency will be attended with an increase in refractive index for a given wave length = $\lambda = 1/\nu$. Such is precisely what has been observed in the experiments described here. It must not be taken for granted, however, that this relation always holds, because further work by the writer on the absorption spectrum of other rare earth salts indicates that it is by no means a general law that all bands shift toward the red with increasing concentration.



6 63 N $Nd(ClO_4)_3$ through
3 mm layer.

Iron arc.

0.1989 N $Nd(ClO_4)_3$ through
100 mm. layer.

Fig. 5.—The 4272 Å. absorption band of $Nd(ClO_4)_3$.

In terms of the contributions to the subject of Fajans and of Ephraim, it appears that we have here to do with a deformation of the outer electron shells of the rare earth ion. Such deformation seems to be brought about by the approach of the negatively charged perchlorate ion and this deformation appears to be communicated in part at least to the inner electron shell believed to be the source of the characteristic absorption bands.

The writer wishes to thank Professor B. Smith Hopkins, in whose laboratory this work was carried on, for the invaluable advice and encouragement which he has from time to time supplied.

Summary

Deformation of the electron shells of the neodymium ion has been investigated from the standpoints of absorption, volume and refraction

changes. Experimental details are given for the analytical work, for the determination of molecular refraction and for the measurement of absorption bands. In the case of neodymium perchlorate, increasing concentration has been found to be associated with an increase in volume and refraction, and a slight shift toward the red of the absoxption bands. Such results agree with deductions from the Clausius–Mosotti theory of dielectrics and are in accordance with recent observations of Fajans and of Ephraim.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

A CHAIN REACTION THEORY OF THE RATE OF EXPLOSION IN DETONATING GAS MIXTURES[1]

BY BERNARD LEWIS[2]

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It is well known that when an explosive gas mixture is ignited at one end of a tube, the initial flame speed, after undergoing a rapid acceleration, acquires a maximum and constant value which does not alter, regardless of the length of the column of gas. Given certain conditions as to temperature, pressure and composition, each gas is characterized by a definite speed of propagation ranging between 1000 and 4000 meters per second. The term detonation wave is usually given to the flame propagated at these velocities.

Theories for the High Rates of Explosions.—Several attempts have been made to account for these high rates of explosions. Berthelot and Vieille[3] compared the speed of a detonation wave to the mean kinetic speed of the molecules in the burned gases. This speed can be readily computed from the temperature attained in the combustion. In many instances the speeds thus calculated differ widely from the experimentally determined velocities of the detonation wave. Dixon[4] likened the speed of the detonation wave in gas mixtures to the velocity of propagation of sound in the same gas at the high temperatures created by the combustion. Although in some cases the velocities calculated agree with those actually found, in others they differ quite widely. It was soon recognized that the "sound-wave theory" was defective and inadequate.[4]

A more satisfactory and hydrodynamical theory was developed independ-

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Read before the American Chemical Society at Atlanta, Georgia, April, 1930.

[2] Physical Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[3] Berthelot and Vieille, *Compt. rend.*, 93, 18, 1881; 94, 149 (1882).

[4] Dixon, Trans. *Roy. Soc.* (London), 184, 97 (1893); *J. Chem. Soc.*, 97, 665 (1910).

ently by D. L. Chapman[6] and E. Jouguet.[6] Their theory utilizes Riemann's and Hugoniot's equations for the propagation of shock waves in fluids where no chemical change occurs. The excellent agreement which Chapman finds seems to be due, at least in part, to the use of specific heats which were derived from the velocity of the detonation wave itself. The early calculations of Jouguet, using old specific heat data, show much better agreement with experiment than when the latest values of specific heats are employed; in fact, the divergences are marked until allowances are made for dissociation of the gases at the high temperatures developed.[7]

Because of the degree of success which the Chapman–Jouguet theory enjoys, it deserves more detailed consideration and exposition. Space will be devoted to this subject elsewhere.[7]

While the following treatment does not possess the distinct advantage of the mathematical theory of Chapman and Jouguet, and for this reason may be said to be more limited in the scope of its application, it does attempt to present pictures of the microscopic molecular mechanisms of propagation from one layer of gas to the next. Por instance, the reaction

$$2CH_4 + 3O_2 = 2CO + 4H_2O$$

involving as it does a quintuple collision, cannot be considered to occur to any appreciable extent in a detonation wave which is traveling some 2500 meters per second. Any picture which is capable of visualizing the individual interactions, and at the same time accounts for the velocity of propagation, is a distinct step in advance.

Obviously, the molecular mechanism should involve some connecting link between the layers of gas through which the explosion front is moving. Furthermore, there is evidence in some cases that the reaction in the latter is incomplete. Accordingly, adopting a kinetic analysis, the writer has sought to account for the high velocities of explosions by making use of the conception of chain reactions which is now generally believed to constitute the means by which explosions occur.[8] This concept permits one to understand how certain interactions may proceed sometimes with velocities enormously greater than can be deduced from a consideration of the initially impressed force. Thus, a single interaction between two molecules may generate a product which reacts with the next suitable molecule it encounters, the process continuing in like manner from layer to layer by reason of regenerated active products through a large number of steps or a chain of reactions.

[5] D. L. Chapman, *Phil. Mag.*, **47**, 90 (1899).

[6] E. Jouguet, *J. de Mathématique*, 347 (1905); 6 (1906); "Mécanique des Explosifs" Paris, 1917.

[7] To be published.

[8] N. Semenoff, *Z. Physik*, **46**, 109 (1927); **48**, 571 (1928); C. N. Hinshelwood and co-workers, *Proc. Roy. Soc.* (London), (1928 and 1929).

Calculation of Rates of Explosions.—The chain theory is adopted in the following attempt to calculate the rates of explosions. The separate links in the chain are usually exothermic in character and of types which occur with reasonable probability. The energy evolved in each step is divided equally among the several degrees of freedom of the products.[9] Some of the products are shot out in the direction of propagation with a velocity corresponding to the energy in their three degrees of translation. The active atom or molecule (hereafter called the "carrier") carries its energy over to the next reaction, accumulating more energy with each succeeding step in the chain. Finally, the energy on the carrier reaches a maximum limit which remains constant, regardless of the number of subsequent steps in the chain. As the time for each single chemical change to occur can be neglected, that part of the maximum energy which is energy of translation determines the velocity of the explosion. It is understood that it is not the same carrier which operates throughout the chain as it proceeds down the length of the tube, but a new and similar one which is regenerated in each successive reaction.

Three typical cases will now be illustrated showing the type of mechanism involved. After an examination of the best available specific heat data at high temperatures and the total number of degrees of freedom possible, the actual average number of degrees of freedom selected for the products in all reactions is as follows: monatomic, 3; diatomic, 8; triatomic, 11.

1. **The Explosion of Hydrogen and Chlorine.**—It is known that in the presence of atoms the reaction proceeds by a long series of steps[10] of the type

$$H + Cl_2 = HCl + Cl \qquad (1)$$
$$Cl + H_2 = HCl + H \qquad (2)$$
$$\text{etc.} \qquad (1)$$

Each reaction generates a product which serves as a reactant in the next step in the chain.

The following thermochemical data are adopted

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[9] As the products consist of mono-, di- and tri-atomic systems and the last two are capable of absorbing energy of vibration and rotation, it was decided, as a first approximation, not to divide the energy according to the mass, that is, in equal momenta The only justification, for the present, for the use of the above method is that when used consistently for many reactions, correct values for rates of propagation can be calculated. At the high temperatures developed where many active degrees of freedom come into play, the energy should be divided amongst all and this seems to offer the simplest method of doing so.

[10] In the photochemical formation of hydrogen chloride the chain lengths have been measured at about a half million [Porter, Bardwell and Lind, THIS JOURNAL, 48, 2603 (1926)]. The chain is terminated by the removal of the atoms by combination with themselves. In the case of an explosion traveling down a tube, the chains must be indefinitely long, because the atoms which are shot out in the direction of propagation continue to meet molecules of chlorine and hydrogen.

$H_2 + Cl_2 = 2HCl + 44$ Kcal.
$H_2 = 2H - 103.5$ Kcal.
$Cl_2 = 2Cl - 57$ Kcal.

Ignition by the spark causes the formation of a certain number of H atoms. Then there follows

$H + Cl_2 = HCl + Cl + 45.25$ Kcal.
(3/11 of 45.25 Kcal. or 12.34 Kcal. is taken up by the Cl atom)
$Cl^{12.34} + H_2 = HCl + H - 1.25 + 12.34 = 11.09$
$H^{3.024} + Cl_2 = HCl + Cl + 45.25 + 3.024 = 48.274$
$Cl^{13.16} + H_2 = HCl + H + 11.91$
$H^{3.25} + Cl_2 = HCl + Cl + 48.50$
$Cl^{13.23} + H_2 = HCl + H + 11.98$
$H^{3.27} + Cl_2 = HCl + Cl + 48.52$
$Cl^{13.235} + H_2 = HCl + H + 11.985$
$H^{3.271} + Cl_2 = HCl + Cl + 48.521$
$Cl^{13.235}$

We shall represent the final carrier of the chain as a chlorine atom possessing 13.235 Kcal. of translational energy. The velocity is given by

$$\tfrac{1}{2} Mv^2 = 13235 \times 4.18 \times 10^7$$

$$v = \sqrt{\frac{2 \times 13235 \times 4.18 \times 10^7}{35.5}} = 1763 \text{ meters per second}$$

The average experimental value for a mixture $H_2 + Cl_2$ is 1765 meters per second.

2. The Explosion of Hydrogen and Oxygen.—The thermochemical data adopted are: heat of formation of OH = +7.5 Kcal.;[11] $H_2 = +103.5$ Kcal.; $H_2O = +57.8$ Kcal.

We shall assume that the spark causes the formation of OH molecules

$H_2 + O_2 = 2OH + 15$ Kcal.
$OH^{7.5} + H_2 = H_2O + H - 1.25 + 7.5 = 6.25$ Kcal.
$H^{1.34} + O_2 + H_2 = H_2O + OH + 117.25 + 1.34 = 118.59$ Kcal.
$OH^{50} + H_2 = H_2O + H + 48.75$
$H^{10.45} + O_2 + H_2 = H_2O + OH + 127.70$
$OH^{53.8} + H_2 = H_2O + H + 52.55$
$H^{11.26} + O_2 + H_2 = H_2O + OH + 128.51$
$OH^{54.1} + H_2 = H_2O + H + 52.85$
$H^{11.33} + H_2 + O_2 = H_2O + OH + 128.58$
$OH^{54.15}$ etc.

3 of the 8 degrees of freedom of OH are translational.

The final carrier is an OH molecule possessing $^3/_8$ of 54.15 or 20.3 Kcal. of translational energy.

$$v = \sqrt{\frac{2 \times 20300 \times 4.18 \times 10^7}{17}} = 3160 \text{ meters per second}$$

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[11] D. S. Villars, Proc. Nat. Acad. *Sci.*, 15, 709 (1929).

The experimental speed for a mixture of $2H_2 + 1O_2$ is 2819 meters per second. Addition of excess oxygen decreases the velocity. This can be explained by the following deactivating reaction

$$H^{11.33} + O_2 = OH + O - 6.25 \text{ Kcal.}$$

The effect of N_2 in lowering the velocity is probably due to inelastic collisions. Addition of excess H_2, on the other hand, increases the speed which may be due to the increased probability of occurrence of

$$OH + H_2 = H_2O + H$$

The maximum speed attained is 3532 meters per second for a $8H_2 + 1O_2$ mixture.

If a value of —3.5 Kcal, is used for the heat of formation of OH[11a] the velocity is 3080 meters per sec.

3. The Explosion of Carbon Monoxide and Oxygen.—The thermochemical data adopted are: heat of formation of CO = +26.5 Kcal.; CO_2 = +94.5 Kcal.; O_3 = —34 Kcal.; O_2 = +131 Kcal.[12]

We shall assume that the spark causes the reaction

$$2CO + O_2 = 2CO_2 + 136 \text{ Kcal.}$$

and that one carbon dioxide molecule collides with a carbon monoxide molecule, the latter emerging with 29 Kcal.

$$CO^{29} + O_2 = CO_2 + O + 2.5 + 29 = 31.5 \text{ Kcal.}$$

$$O^{6.75} + O_2 \xrightarrow{\text{CO or } O_2} O_3 + O_2 + 31.5 + 6.75 = 38.25 \text{ Kcal.}$$

(This reaction takes place in triple collision)

$$O_3^{22.13} + CO + CO = 2CO_2 + O + 104.5 + 22.13 = 126.63 \text{ Kcal.}$$

$$O^{15.2} + O_2 \xrightarrow{\text{CO or } O_2} O_3 + O_2 + 46.7$$

$$O_3^{27.03} + CO + CO = 2CO_2 + O_2 + 131.53$$

$$O^{15.78} + O_2 \longrightarrow O_3 + O_2 + 47.28$$

$$O_3^{27.38} + CO + CO = 2CO_2 + O + 131.88$$

$$O^{15.83} + O_2 \longrightarrow O_3 + O_2 + 47.33$$

$$O_3^{27.40} + CO + CO = 2CO_2 + O + 131.90$$

$$O^{15.83} + O_2 \longrightarrow O_3 + O_2 + 47.33$$

$$O_3^{27.40}$$

Three of the eleven degrees of freedom of O_3 are translational. The translational kinetic energy is 7.47 Kcal. and the corresponding velocity is

$$v = \sqrt{\frac{2 \times 7470 \times 4.18 \times 10^7}{48}} = 1140 \text{ meters per second}$$

The experimental average of Berthelot's and Dixon's results is 1135 meters per second. Should the foregoing mechanism be modified so that the fourth reaction is split up into two steps, namely

$$O_3 + CO = CO_2 + O_2$$

[11a] R. Mecke, *Z. physik. Chem.*, *7B*, (1930).

[12] G. Herzberg, *ibid.*, 4B, 223 (1929); J. Kaplan, *Phys. Rev.*, 35, 436 (1930); R. T. Birge, *Trans. Faraday Soc.*, *25*, 707 (1929); R. Mecke, *Naturwiss.*, 17, 996 (1929).

and

$$O_2 + CO = CO_2 + O$$

the final velocity turns out to be 1100 meters per second, which is in good agreement with Berthelot's average of 1103 meters per second. All other possible mechanisms give final velocities which deviate by over 150% from the observed values.

It can be shown that whatever the initial reaction caused by the ignition, or the initial amount of energy therefore on the carbon monoxide molecule, the final results are identical provided that the same subsequent mechanism is adhered to. For instance, if the ignition brings about the reaction

$$CO + O = CO_2 + 133\ 5$$

followed by

$$CO_2^{133.5} + CO = CO^{56.2} + CO_2^{77.3}$$
$$CO^{56.2} + O_2 = CO_2 + O + 2.5 + 56.2 = 58.7 \text{ Kcal.}$$
$$O^{12.58} + O_2 \xrightarrow{\text{CO or } O_2} O_3 + O_2 + 31.5 + 12.58 = 44.08$$
$$O_3^{25.5} + CO + CO = \text{etc.}$$

the final O_3 carrier will still possess 27.40 Kcal. of energy. Furthermore, should the ignition process impart a large amount of energy to the initial carriers, causing them to travel with a velocity greater than the final constant value, the chain mechanism indicates how these highly energized carriers are deprived of some of their energy. The final carriers will possess energy corresponding exactly to the velocity characteristic of the mixture. This deceleration of the detonation wave has been shown by C. Campbell and D. W. Woodhead[13] in the case of the ignition of a hydrogen–oxygen mixture by another hydrogen–oxygen mixture possessing a greater characteristic velocity. It is possible, though not certain, that photographs published by W. A. Bone and R. P. Fraser[14] can be interpreted in this light.

It is noteworthy that the chain theory explains the acceleration or deceleration of the explosion wave front to the final constant velocity characteristic of the mixture.

In proceeding as above, the writer has imposed conditions which would tend to lower the calculated results. However, for a given mechanism and carrier the velocity calculated represents a maximum—that is, on the basis that each reaction in the chain occurs before the carrier is deactivated.[15]

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[13] Campbell and Woodhead, J. Chem. *Soc.*, 3010 (1926).

[14] Bone and Fraser, *Trans.* Roy *Soc.*, (London) **A228,** 197–234 (1929), Plate 10, No. **37,** Plate 11, No. 38.

[15] The substitution of inert gases such as helium and argon for an excess of one of the constituents would normally be expected to lower the rate. We have shown,[7] however, that helium causes a marked increase in the rate when it is added to a mixture of $2H_2$ and $1O_2$, whereas the addition of argon lowers it. If helium and argon behaved differently in the transfer of energy by collision, the former giving up energy of translation to the carrier and the latter removing energy, this could be accounted for. De-

This is directly comparable with the experimental values about to be given in the accompanying table, since it contains those values for the optimum composition of a combustible gas mixture which gives the maximum velocity. For instance, the maximum value for the H_z–02 explosion is for an $8H_2 + O_2$ mixture.

Attention is directed to the fact that the final carrier in a given mechanism has been rather arbitrarily selected. For instance, in the H_2–Cl_2 explosion the atomic hydrogen carrier indicates a velocity of 5200 meters per second. This offers no difficulty in accounting for the high rate of the explosion. The case would be different were no carrier present possessing a final velocity equal to at least the experimental velocity of the detonation wave. The carriers listed in Table II were selected because the velocities calculated from them are close to the true values. In a few cases they represent the highest velocity carrier. If the microscopic chemical process was the only factor which determined the velocity of the detonation wave, it would be difiicult to understand why the velocity is not that of the fastest carrier. It is possible that a fusion of the present theory and the Chapman–Jouguet theory in a manner indicated elsewhere[7] is desirable for an understanding of two striking phenomena in explosions, namely, the high speed of the detonation wave and the extreme rapidity of chemical reaction in the wave front.

Before presenting the table of results it may prove of interest to include a few mechanisms for the reactions occurring in the explosion wave front for other explosions; these are given briefly in Table I.

TABLE I

REACTION MECHANISMS

Explosion	Mechanism adopted
CH_4 and O_2	$O + O_2 + CH_4 = C + 2H_2O + O$
C_2H_4 and O_2	$O + O_2 + C_2H_4 = 2C + 2H_2O + O$ $O + O_2 + C_2H_4 = CO_2 + 2H_2 + C + O$
H_2 and N_2O	$H + N_2O = N_2 + OH$ $OH + Hz = H_2O + H$
C_2H_6 and O_2	$O + O_2 + C_2H_6 = 2C + 2H_2O + H_2 + O$
CS_2 and O_2	$O_2 + CS_2 = SO_2 + C + S$ $S + 0\,2 \xrightarrow{O_2} SO2 + O_2$
O_3	$O + O_3 = 202$ $0\,2 + O_3 = 202 + O$

Table II contains a summary of calculated and experimental velocities. It is not maintained that the mechanisms selected are correct. Suffice it to remark that they are plausible and possible, and that the carriers selected

spite the differencein their atomic weights, there is no real evidence for this assumption. On the other hand, it will be shown that the inverse behaviors of helium and argon are readily explained by the Chapman–Jouguet theory (cited).

give the correct velocities while others give values far removed from those found. The experimental values are those of Dixon and others.[16]

TABLE II

SUMMARY OF CALCULATED AND EXPERIMENTAL VELOCITIES

Explosion	Carrier	Vel. calcd., meters/sec.	Vel. observed, meters/sec.	Deviation, %
$H_2 + O_2$	OH	3160	3532	−10.5
$H_2 + Cl_2$	Cl	1763	1765	−0.11
$CO + O_2$	O_2	1140	1135	+0.44
$C_2N_2 + O_2$	N	2780	2728	+1.9
$CH_4 + O_2$	O	2480	2513	−1.3
$C_2H_4 + O_2$	O	2530	2559	−1.1
$C_2H_2 + O_2$	O	2947	2941	+0.20
$NH_3 + O_2$	O	2435	2390	+1.9
$H_2 + N_2O$	OH	2840	>2732	+<3.9
$C_2H_2 + N_2O$	O	2635	2580	+2.1
$C_2H_2 + NO$	O C N_2	2773 3435 2390 } 2866	2850	+0.6
$C_2H_6 + O_2$	O	2010	2363	−15.0
$CS_2 + O_2$	O_2	1960	1802	+8.8
$2O_3 \longrightarrow 3O_2$	O_2	2240	Not measured; calcd. by Jouguet theory, 2123	

In some explosions it is difficult to picture a mechanism in the flame front because there is little or no knowledge concerning the degree to which the reaction progresses in it. Where marked deviations below the observed values occur it is possible that some unknown mechanism is in operation. Despite this, however, the concordance is exceptionally good in most cases

Summary

An attempt has been made to calculate the velocity of propagation of gaseous explosions employing the concept of reaction chains. Fourteen explosive mixtures were investigated, mechanisms developed and the calculated velocities compared with known experimental values. The agreement is exceptionally good in most cases.

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[16] See Bone and Townend, "Flame and Combustion in Gases," 1927, pp. 511–518.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

AN APPARATUS FOR THE DETERMINATION OF MELTING POINTS

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A comprehensive summary of methods and devices for the determination of the melting points of organic substances is given in Oesper's translation of Lassar-Cohn's "Organic Laboratory Methods," with notes and comments by Roger Adams. None of the methods there described is rapid, several of them are of doubtful accuracy, and all of them, with perhaps the exception of the Maquenne block, fail to give correct results if the substance tends to decompose before it reaches the melting point.

One of the most accurate and rapid methods for the measurement of temperature is by a thermocouple used in conjunction with a potentiometer. An apparatus that employs this combination, and with which the melting points of substances, either organic or inorganic, within the range from room temperature to 300°, may accurately be determined in a few seconds, is shown in Fig. 1. A is a bar of very pure[1] copper 61 cm. long. It is square, 25 mm. × 25 mm., through about 53 cm. of its length and the remaining 8 cm. is turned down to a cylindrical shoulder 2 cm. in diameter. This shoulder, S, is first covered with a thin layer of asbestos paper, and then 18 turns of nichrome ribbon, $^1/_{16}$ in. × 0.0325 mm., are wrapped around it. The ends of the ribbon are fastened to the two binding posts B and C. The coil of ribbon is covered with a layer of asbestos cement about 6 mm. thick. A current, either a. c. or d. c., passed through this ribbon, heats the bar A, and is so adjusted by suitable resistance that the range of temperature of the bar between the hotter and cooler ends includes the temperatures of the melting points of the substances under examination.

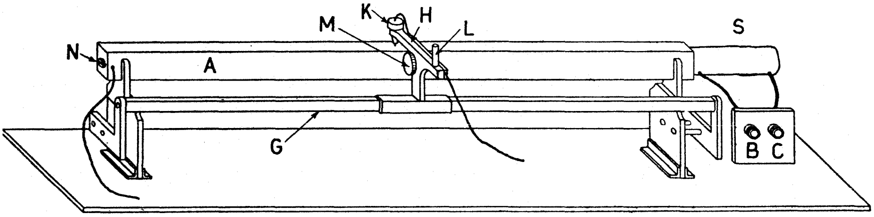

Fig. 1.

Parallel with the copper bar A is a guide rod G that carries the pivoted arm H to which is fastened an insulated wire of constantan. The end

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[1] Spectroscopic examination showed that it contained only minute traces of aluminum, magnesium and iron.

of this wire passes through the head K of the arm, and the exposed end of the wire is lightly but firmly pressed down upon the surface of A by a spiral spring in L, when the button M is turned to the left. The arm is raised from the bar and held there, by turning the button M to the right.[2]

Copper and constantan were employed as the thermoelectric pair because in respect to thermoelectric power, homogeneity and permanence,[3] this couple is admirably adapted to measurements between room temperature and 400°. The constantan wire that was used is No. 20, diameter 0.08 mm.

The further end of the constantan wire, and a pure copper wire, 0.08 mm. in diameter, which is fastened to the cooler end of A by the binding post N, are connected to a potentiometer.[4] No calibration of the heated bar A is necessary. It need only be brought at some point (any point) to the temperature at which the substance under examination will melt. The differences of temperature between the two ends of **A** were found to be as follows:

Current through heating coil around S, amp.	Hotter end,[5] °C.	Cooler end, °C.
4	90	63
5	131	87
6	140	95
7	176	107
8	233	131
9	250	150
10	302	167

A determination of the melting point of a substance is made as follows. When the bar A has been brought to such a temperature that somewhere (anywhere) along its length the melting point of the substance under

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[2] To ensure satisfactory construction of the apparatus, application for a patent on the device has been made.

[3] See White, THIS JOURNAL, 36, **1856, 1868, 2011, 2480 (1914).**

[4] The potentiometer was a double-range potentiometer indicator of the Leeds and Northrup Co., scales 0–16 millivolts, and **0–80** millivolts, their catalog No. **8657-B.** This instrument is equipped with a manual cold junction compensator that is set by means of a dial to the millivolts corresponding to the temperature, as read from a thermometer, of the cold junction of the thermocouple that is being employed. With a potentiometer not fitted with such a compensator the cold junction of the thermocouple must be maintained at 0°.

[5] Melting points as high as 320° have been determined with the bar, but it is not advisable to hold the bar at a temperature above 275° for any considerable length of time because superficial oxidation of the copper may result. The thin layer of oxide does not, however, appreciably affect the determination, if the constantan contact is firmly pressed down with the finger. The bar can easily be cleaned with a "metal polish," several satisfactory kinds of which are on the market. Bars of metals other than copper, for use with substances of melting points above 300°, are now being tested.

examination is reached, particles of the finely-ground substance are dropped along the surface of the bar from a small spatula or knife blade. The arm H, with the point of the constantan wire raised, is slid along the guide rod, and by turning the button M the end of the constantan wire is brought down upon the bar exactly on the line separating the melted from the unmelted substance. This line is a very sharp one. The potentiometer is then read, and the temperature corresponding to the observed current is taken from the standard calibration tables.[6] With this apparatus readings can be made that are accurate within 10 microvolts = 0.25°.

The arm H is then raised by turning M, the surface of the bar A is wiped off with a clean cloth, and the apparatus is ready for the next determination. The whole manual operation need not take longer than thirty seconds, and the operation is so rapid that accurate results are obtained even when the substance dissociates upon brief heating.

Uniformity of Results with Bar A at Different Temperatures.—The melting point of acetanilide was determined at different points along the bar with the hotter end of the bar held at four different temperatures, 125, 150, 180 and 200°. The observed melting point was the same (114.25°) in all cases.

TABLE I

DETERMINATIONS OF MELTING POINTS OF VARIOUS COMPOUNDS WITH ELECTRIC BAR

Organic Compounds

	Literature			Found
Benzophenone			48.5	48.2
p-Nitrotoluene		51.3	51.5	51.5
Palmitic acid		63	64.0	64.1
p-Bromo-aniline		66.0	66.4	66.5
Stearic acid		69.0	66.4	69.8
a-Nitro-aniline		71.0	71.5	71.6
Naphthalene		80.0	80.1	80.2
Triphenylmethane		92	92.5	92.5
Acetanilide		114.0	114.2	114.25
Mandelic acid	117.8	118	118.2	118.5
Benzoic acid		121.1	121.0	121.1
p-Bromonitrobenzene		66	66.4	66.5
Urea		132.2	132.7	132.8
Cinnamic acid			133.0	133.2
m-Nitrobenzoic acid	140	141.4	141.6	141.6
p-Bromo-acetanilide	165.4	167	168.0	166.0
Hippuric acid		187.0	187.5	187.3
p-Hydroxybenzoic acid			213.0	213.2
Caffeine			234.0	234.4

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[6] Bulletin No. 170, Bureau of Standards, "Pyrometric Practice," p. 309. Also in "International Critical Tables," 1926, Vol. I, p. 58.

TABLE I *(Concluded)*

	Literature			Pound
Metallo-organic Compounds				
Diphenyl mercury	120	121.8	124.5	124.6
o-Nitrophenyl mercuric chloride			182.0	182.0
α-Naphthyl mercuric chloride	188–189		188	188.9
Ethyl mercuric chloride			192.5	192.7
Inorganic Compounds				
Ammonium nitrate			169.6	169.6
Silver nitrate		209	212	211.4

Determination of Melting Points of Substances that Readily Dissociate or Sublime when Heated.—In the tabulation of melting points of organic substances in the "International Critical Tables," Vol. I, pp. 176–275, the value for many compounds is followed by a "d," meaning that the substance decomposes when being heated to determine its melting point by the method that was employed. These values cannot, of course, be regarded as the correct melting points of the compounds. When determined by the "capillary tube" method, the apparent melting point of a substance that decomposes when being heated may vary between wide limits, the variation depending upon the procedure employed. The rate of heating is one of the chief causes of these differences. Some substances of this character were tested with the apparatus here described, and in every case definite melting points were obtained, and several determinations of each were practically identical.

TABLE II

MELTING POINTS OF SOME SUBSTANCES THAT READILY DECOMPOSE WHEN HEATED

Substance	"Int. Crit. Tables," °C.	Electric bar,[7] °C.
Phthalic acid	191 d.	228.5
Alloxan	170 d.	210
Barbituric acid	240 d.	250
Glycine	232 d.	297.2
Fumaric acid	287 d.	297

The melting point of phenyl boric acid is given by Pace[8] as 204°. Recent determinations in the Cornell Laboratory by the "capillary tube" method gave 210–212°. Inasmuch as the anhydride of the acid is formed when the acid is heated, the melting points were those of mixtures of the anhydride and the acid. With the electric bar several determinations of phenyl boric acid agreed exactly at 222.5'.

Speed of Determinations of Melting Points by Different Methods.—In these determinations the melting points were not known to the operator.

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[7] The compounds were not of high purity; the results are therefore merely illustrative of the applicability of the method to such cases, and are not to be regarded as the correct melting points.

[8] Pace, *Atti accad. Lincei*, **10**, 193 (1929).

If they had been, the determinations with the capillary tube and Maquenne block might have taken appreciably less time.

TABLE III

SPEED OF DETERMINATIONS OF MELTING POINTS BY DIFFERENT METHODS

Substance	I	II	III	IV	Time for the 4 detns.
Capillary tube method	118.5	121	167	91	1 hour
Maquenne block	118.5–119	120.5	166–167	91–92	4 hours[a]
Electric block	118.5	121.1	166	92.5	2 minutes
M. p. in literature	118.5	121.1	165.4	92 5	

[a] Because of difficulty in controlling the temperature of the bar.

Summary

This article describes a device for the measurement of the melting points of substances, particularly of organic substances, up to temperatures of about 300°. With the apparatus, melting points can be determined in about thirty seconds with an accuracy of about 0.25'.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

A CONTRIBUTION TO THE STUDY OF CHAIN REACTIONS. (A) REMARKS ON A PAPER BY LENHER AND ROLLEFSON ON THE KINEMATICS OF PHOSGENE. (B) THE .MECHANISM OF THE FORMATION AND DECOMPOSITION OF ETHYLENE IODIDE

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Introduction

Recently a paper by Polissar[2] on the kinetics of the thermal decomposition of ethylene iodide appeared in THIS JOURNAL. The decomposition was carried out in the presence of iodine in carbon tetrachloride solution. The interesting result of this careful investigation is that the velocity of the decomposition can be represented by the equation

$$-\frac{d[C_2H_4I_2]}{dt} = k[C_2H_4I_2][I_2]^{1/2}$$

This equation is, as mentioned by Polissar, similar to that of the phosgene decomposition, which is given below

$$-\frac{d[COCl_2]}{dt} = k[COCl_2][Cl_2]^{1/2}$$

Polissar, in his discussion of results, seems to have misunderstood the mechanism of the phosgene decomposition and his interpretation of the

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[2] M. J. Polissar, THIS JOURNAL, 52,956 (1930).

heat of activation in chain reactions is not very clear. These questions will be discussed in the present communication. Also, a mechanism for the formation and decomposition of ethylene iodide will be given. This mechanism, without any artificial assumptions, leads to the observed kinetic equation.

Remarks on the Phosgene Reaction.—The kinetics and photochemistry of phosgene have been intensively investigated by Bodenstein **and** co-workers.[4] All this previous work together with recent unpublished investigations will be thoroughly discussed in a forthcoming publication.' In this paper a theory will be given which enables one to represent quantitatively the thermal and photo-kinetics of this complicated reaction. Also, a mechanism will be given by which the carbon dioxide formation (sensitized by chlorine) can be interpreted. This is closely related to the phosgene reaction.

The basis of the mechanism of the phosgene reaction is that which has been given by Bodenstein, Lenher and Wagner.[3]

$$\begin{aligned}
Cl_2 + h\nu &\longrightarrow Cl + Cl && (1)\\
Cl + CO &\longrightarrow COCl \quad \left.\right\} \text{Equilibrium} && (2)\\
COC &\longrightarrow CO + Cl && (3)\\
CO + Cl + Cl_2 &\longrightarrow COCl_2 + C && (4)\\
Cl + COCl &\longrightarrow CO + Cl_2 && (5)
\end{aligned}$$

This mechanism has recently been criticized by Lenher and Rollefson,[5] who substitute another mechanism. In the following it will be shown that their objections are not substantiated and that their proposed mechanism is highly improbable.

(I) In the mechanism proposed by Bodenstein, Lenher and Wagner Reactions 2 and 3 proceed at such a velocity that the COCl concentration is always equal to its equilibrium concentration. Equation 4 has only a formal meaning. It can, as was pointed out by Bodenstein, Lenher and Wagner,[6] be replaced by the reaction

$$COCl + Cl_2 \longrightarrow COCl_2 + Cl$$

assuming, of course, that the COCl equilibrium is not disturbed. Evidently this has been overlooked by Lenher and Rollefson, who say that they cannot understand why COCl should react with oxygen and not with chlorine. This is not required at all. In order to explain the experimental fact that the phosgene reaction is strongly inhibited by small amounts of oxygen, it has to be assumed that the COCl reacts much faster with oxygen than with chlorine. There does not seem to be any difficulty in

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[3] (a) M. Bodenstein and Plaut, *Z. physik. Chem.*, 110,399 (1924); (b) M. Bodenstein, *ibid.*, 130,422 (1927); (c) H. J. Schumacher, *ibid.*, 129,241 (1927); (d) M. Bodenstein and Onoda, *ibid.*, 131, 153 (1927); (e) M. Bodenstein, S. Lenher and C. Wagner, *ibid.*, 3B, 459 (1929).

[4] M. Bodenstein, H. J. Schumacher and G. Stieger, *ibid.*, in press (1930).

[5] Lenher and Rollefson, THIS JOURNAL, 52, 500 (1930).

[6] Bodenstein, Lenher and Wagner, Ref. 3, p. 470.

this conception and Lenher and Rollefson have to make the same assumption in their own scheme in order to account for the inhibiting influence of oxygen.

(II) Lenher and Rollefson see difficulty in that the COCl always has to be at its equilibrium concentration. In reference to this the following can be said. The heat of formation of COCl from CO and Cl can be estimated to be about 5 cal. Indeed the formation of COCl can only occur in a three-body collision, which means that the quasi-molecule COCl has, in order to be stabilized, to collide with another molecule within its life of about 10^{-13} sec.[7] But except in the case of very low pressures three-body collisions are so frequent that the velocity of formation is sufficient. In consequence of the small heat of formation the COCl is decomposed fast enough. Therefore, there is no reason to throw out the existence of the COCl equilibrium.

(III) The third point in the objections of Lenher and Rollefson, namely, that reactions of Type 4 take place very seldom, was partly settled under (I). There we have shown that the above Reaction 4 can be substituted by the reaction

$$COCl + Cl_2 \longrightarrow COCl_2 + Cl$$

It is however to be emphasized that reactions of Type 4 are quite possible and, in fact, the probability of such a reaction can be great,[8] although of course, Reaction 4 has only a formal meaning, as has been mentioned before.

The above indicates that the objections of Lenher and Rollefson are not valid. These authors propose the mechanism

$$Cl_2 + h\nu \longrightarrow Cl + Cl \tag{1}$$
$$CO + Cl + X \longrightarrow COCl + X \tag{2}$$
$$COCl + Cl_2 \longrightarrow COCl_2 + Cl \tag{3}$$
$$COCl + Cl \longrightarrow CO + Cl_2 \tag{4}$$

According to this the COCl is not present in its equilibrium concentration. In order to obtain the right equation for the reaction velocity it has to be postulated that COCl can be formed only if it is stabilized by a collision with a chlorine molecule. This means that X in Equation 2 is equal to Cl_2. All other gases are not supposed to have any influence on the process.

To this it can be said that the law for the reaction velocity for the phosgene formation is still valid if Cl_2 compared with other gases (CO, $COCl_2$, CO_2) is present in small concentration (1 to 50 and less). In order to exclude the influence of these gases on Reaction 2 it has to be assumed that chlorine is several hundred times as efficient as these gases. It has

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[7] Herzfeld, *Ann. Physik*, 59,635 (1919).

[8] Lenher and Rollefson believe that these reactions are improbable and make reference to a paper by Frenkel and Semenoff [Z. *Physik*, 48,216 (1928)]. The probability given by these authors, as has been shown by Jost [*Z. physik. Chem.*, 3B, 126 (1929)] is too small by a factor of about 10^5.

to be emphasized that such an assumption is contradictory to all known experimental facts. Lenher and Rollefson cite as proof of their theory the specific effect of different gases on the quenching of fluorescence radiation. Apart from the fact that CO and CO_2 quench the fluorescence generally very well, it must be pointed out that the three-body collision is quite a different process. As is well known, in a three-body collision the third molecule has to take up only that part of the energy of the quasi-molecule which separates it from a stable state. This can be a very small amount and normally is of the order of magnitude of the mean kinetic energy of molecules. Only monatomic gases are usually relatively inefficient.[9] Polyatomic gases are usually in their efficiency as third bodies only different by a factor smaller than three.[10] It does not seem probable that chlorine should be several hundred times as efficient as the other polyatomic gases, so it must be said that the mechanism proposed by Lenher and Rollefson is rather improbable.

Discussion of Polissar's Interpretation of the Heat of Activation of the Phosgene Reaction.—The heat of activation of a bimolecular reaction, as determined from the temperature coefficient, is the minimum energy in excess of the average energy, which any two molecules must have in order to react upon collision.[11] The question of whether the activation energy is to be considered as internal or as kinetic energy will not be discussed here, there being already considerable literature on this point.[12]

In the case of chain reactions, of course, the value of Q, the heat of activation determined from the temperature coefficient, loses its simple physical significance. In such reactions the value of Q is made of the Q' of the reactions forming the different stages of the total reaction. Bodenstein and his co-workers[13] have published examples of the method of calculation in such cases.

Now the thermal decomposition of phosgene is a typical chain reaction,[14] the heat of activation of the various stages having been calculated by Bodenstein and Plaut. Polissar does not consider this mechanism. His value of 24 Cal. for Q'' corresponds to the reaction

$$COCl_2 + Cl \longrightarrow COCl + Cl_2$$

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[9] W. Jost, Z. *physik. Chem.*, **3B,** 95 (1929).

[10] H. J. Schumacher, THIS JOURNAL, 52, 2377 (1930).

[11] J. A. Christiansen, *Proc. Cambridge Soc.*, [XXIII] 4, 438 (1926).

[12] Kallman and London, *Z. physik. Chem.*, **2B,** 207 (1929); Fowler, "Statistical Mechanics," 1929, p. 462; H. J. Schumacher and G. Sprenger, *Z. physik. Chem.*, 6B, 446 (1930); Arne Olander, *ibid.*, 7,311 (1930); *H.* J. Schumacher, *ibid.*, **8B,** 218 (1930); L. S. Kassel, *Phys. Rev.*, 35, 261 (1930); D. S. Villars, *ibid.*, 34, 1063 (1929); THIS JOURNAL, 52,1733 (1930).

[13] M. Bodenstein, E. Padelt and H. J. Schumacher, Z. *physik. Chem.*, **5B,** 209 (1929); H. J. Schumacher and G. Sprenger, *ibid.*, 2B, 267 (1929).

[14] J. A. Christiansen, "Reaktionskinetiske Studier," Priors Hofboghandel, Kopenhagen; M. Bodenstein and Plaut, *Z. physik. Chem.*, 110,400 (1924).

The reaction between Q" and the heat of dissociation of phosgene is such that the sum of Q" and the dissociation energy of COCl must be equal to the dissociation energy of $COCl_2$. It is assumed that reaction takes place in every collision, when the reaction is exothermic. Only then the relation is correct Q_{COCl} has a value of about 5 Cal.[3e]

The ease with which the second Cl atom is split off from $COCl_2$ is explained by the fact that when the Cl atom is removed from COCl the carbon atom passes back from the (^5S) to the (^3P) state.[15] Simultaneously, energy is liberated corresponding to the energy difference of these two states. This energy is just of the right order of magnitude.[15b]

The Mechanism of the Decomposition of Ethylene Iodine Catalyzed by Iodine.—As Polissar found, the decomposition of $C_2H_4I_2$ catalyzed by I_2 takes place according to the equation

$$-\frac{d[C_2H_4I_2]}{dt} = k[C_2H_4I_2]\ [I_2]^{1/2}$$

Consequently, the equation for the synthesis **is**

$$+\frac{d[C_2H_4I_2]}{dt} = k'[C_2H_4][I_2]^{3/2}$$

The following scheme is given by Polissar

(a) Synthesis

$$\begin{array}{rcll} I_2 & \rightleftarrows & I + I & (1) \\ I + I_2 + C_2H_4 & \longrightarrow & C_2H_4I_2 + I & (2) \end{array}$$

(b) Decomposition

$$\begin{array}{rcll} I_2 & \longrightarrow & I + I & (1) \\ I + C_2H_4I_2 & \longrightarrow & C_2H_4 + I + I_2 & (2) \end{array}$$

Reaction 2 has evidently only formal but no chemical significance. By analogy with the mechanism of the phosgene reaction, the following mechanism is suggested

(a) Synthesis

$$\begin{array}{rcll} I_2 & \rightleftarrows & I + I & (1a) \\ I + C_2H_4 & \longrightarrow & C_2H_4I & (2a) \\ C_2H_4I & \longrightarrow & C_2H_4 + I & (3a) \\ C\ H_4I + I_2 & \longrightarrow & C_2H_4I_2 + I & (4a) \end{array} \quad \text{(2a), (3a)}\ \Big\}\ \text{equilibrium}$$

(b) Decomposition

$$\begin{array}{rcll} I_2 & \rightleftarrows & I + I & (1b) \\ C_2H_4I_2 + I & \longrightarrow & C_2H_4I + I_2 & (2b) \\ C\ H_4I & \longrightarrow & C_2H_4 + I & (3b) \\ C_2H_4 + I & \longrightarrow & C_2H_4I & (4b) \end{array} \quad \text{(3b), (4b)}\ \Big\}\ \text{equilibrium}$$

The rate of the synthesis is determined by Reaction 4a and that of the decomposition by 2b. Both iodine atoms and C_2H_4I molecules should be present throughout in their equilibrium concentrations. If such is the case, the expression for the synthesis becomes

$$+\frac{d[C_2H_4I_2]}{dt} = k_4 \times K_{C_2H_4I} \times K_{I_2}{}^{1/2} \times [C_2H_4][I_2]^{1/2} \qquad (I)$$

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[15] (a) F. London, *Z. Physik*, **46**, 455 (1928); (b) R. Mecke, *Z. physik. Chem.*, **7B**, 108 (1930).

where $K_{C_2H_4I} = k_2/k_3$ and K_{I_2} are the equilibrium constants of the corresponding reactions. For the decomposition we get

$$-\frac{d[C_2H_4I_2]}{dt} = k_2K_{I_2}^{1/2}[C_2H_4I_2][I_2]^{1/2} \qquad \text{(II)}$$

These correspond with the equations found by experiment. From the form of the equation it is seen that iodine atoms can recombine only according to Reaction 1 but not according to the equation $C_2H_4I + I \longrightarrow C_2H_4 + I_2$. That is to say, the concentration of C_2H_4I must be very small. This will be the case when the heat of the reaction $C_2H_4 + I \longrightarrow C_2H_4I$ is very low.

The reaction $I + I \longrightarrow I_2$ depends on three-body collisions. In solution it should be practically independent of pressure, or at least the effect will be small.

Polissar determined experimentally the heat of decomposition of ethylene iodide into ethylene and iodine, the velocity constants of the decomposition and their dependence on temperature. Bodenstein[16] has already measured the equilibrium between iodine and iodine atoms, and sufficient data are therefore available for the calculations of heat of activation of the component reactions in the decomposition of ethylene iodide.

According to Polissar, for T = 425° the velocity constant $k = 710 \times 10^{-4}$; for T = 415°, $k = 278 \times 10^{-4}$. From these figures the apparent heat of activation at this temperature is 32.800 cal. = **Q.** It follows from Equation II that $k = k_2\sqrt{K}$. Consequently $32.800 = Q'' + \frac{1}{2}Q'$, when Q'' is the heat of activation of Reaction 2b and Q' is the heat of dissociation of iodine at 420°. According to Bodenstein and Stark[16]

$$Q' = 35.400 + 3.5T - 0.0019T^2$$

i. e., $Q'_{420} = 36.600$ Cal., and the value of Q" so obtained

$$Q'' = 32.800 - 18.300 = 14.500 \text{ Cal.}$$

Since Polissar's values of the velocity constants are not very exact, the same calculations have been repeated for 405° and 395°, and the average value of Q" taken.

$$k_{405°} = 119 \times 10^{-4};\quad k_{395°} = 47.2 \times 10^{-4}$$

The corresponding values are

$$Q_{410°} = 28.300 \text{ Cal. and } Q''_{410°} = 28.300 - 18.250 = 10.050 \text{ Cal.}$$
$$Q_{400°} = 28.00 \text{ Cal. and } Q''_{400°} = 28.000 - 18.250 = 9.750 \text{ Cal.}$$

Taking the average and neglecting the dependence of Q" on temperature, the value of **Q"** for the reaction

$$C_2H_4I_2 + I \longrightarrow C_2H_4I + I_2$$

comes out to be

$$Q''_{410°} = 11.500 \text{ Cal.}$$

This value of Q" is correct to about 2 cal.

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[16] M. Bodenstein and Stark, Z. *Elektrochem.*, 16,961 (1910).

According to a general principle, due to Trautz, the heat of reaction may be expressed as the difference of the heats of activation of the forward and the reverse reaction. In the case of exchange reactions, in which atoms or radicals take part, reaction takes place in every collision, if the process is exothermic. Some exceptions[17] to this rule, given by Polanyi,[18] have recently been found, but it can nevertheless be taken as generally valid. Assuming it in the case of the reaction between $C_2H_4I_2 + I$ and of the reverse reaction $C_2H_4I + I_2$, Q'' will then represent the heat of this reaction.

$$I_2 + C_2H_4I \longrightarrow C_2H_4I_2 + I + 11.500 \text{ Cal.}$$

As is evident by comparing Equations I and II, $Q_{C_2H_4I}$ will have the low value of 0.200 Cal., since Polissar gave the heat of the total reaction as 11.300 Cal. The value of $Q_{C_2H_4I}$ is also correct only to a few calories. A low value of Q is, however, to be expected. Having obtained this, the heat of activation has been determined for every reaction which takes part in the formation and decomposition of $C_2H_4I_2$ in the presence of iodine.

Calculations of Strength of Binding from Thermal Data.—From the thermal data we can calculate the value of the C—I linkage in $C_2H_4I_2$ and of the difference in energy between the carbon double bond in C_2H_4 and the C—C bond in $C_2H_4I_2$. In the dissociation of $C_2H_4I_2$ into C_2H_4 and I_2, two C—I linkages are broken, one C=C linkage and one iodine molecule being produced. This is expressed by the equation

$$2\,(C{-}I) = C{=}C + I_2 + Q$$

where Q = 11.300 Cal., I_2 = 36.500 Cal. is the heat of formation of I_2 at the temperature in question and C=C is the energy difference between the single and the double carbon linkage.

$$2C{-}I = C{=}C + 47.8 \text{ Cal.} \qquad \text{(A)}$$

We have calculated

$$C_2H_4I \longrightarrow C_2H_4 + I - 0.2 \text{ Cal., } i.\,e.,$$
$$C{-}I = C{=}C - 0.2 \text{ Cal.} \qquad \text{(B)}$$

and from A–B

$$C{-}I = 48 \text{ Cal.}$$

That is, the value of the linkage between carbon and iodine is 48 Cal., which is higher than the value determined from the thermal data. Grimm[19] gave an average value for the C—I linkage of 44 Cal. Bates and Andrews[20] give 40 Cal., but in the value we obtained, a part of the excitation energy of a (^3P) to a (^5S) carbon atom is included.

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[17] G. B. Kistiakowsky, This journal, 52, 1868 (1930); H. J. Schumacher, *ibid.*, 52, 2377 (1930).

[18] Beutler and Polanyi, *Z. physik. Chem.*, **1B**, 3 (1928); Bogdandy and Polanyi, *ibid.*, **1B**, 21 (1928); Polanyi and Schay, *ibid.*, **1B**, 30 (1928).

[19] Grimm, "Handbuch der Physik," Vol. XXIV, p. 536.

[20] Bates and Andrews, *Proc. Nat. Acad. Sci.*, *14*, 124 (1928).

For the energy difference between C=C and C—C the value 48.2 Cal. is obtained, whereas Grimm gave an average value of 54.

It is now easily understood why the second iodine atom splits off so readily from $C_2H_4I_2$, for this process is coupled with the liberation of energy accompanying the formation of the C=C bond.

In the case of phosgene it was the transition of the C atom from the (^5S) to the (^3P) state which made the Cl atom readily removable. The energy difference of these two states, as can be calculated from kinetic data,[3e] has the value of 74 Cal., in agreement with the value of 60–100 Cal. given by Mecke.[15b]

The author wishes to express his thanks to Dr. H. J. Emeléus and Dr. G. I. Lavin of this Laboratory for translating the paper into English.

Summary

1. An article of Lenher and Rollefson on the mechanism of the phosgene reaction is discussed.

2. A mechanism of the reaction between iodine and ethylene iodide and iodine and ethylene is given, and the heats of activation of the component reactions are calculated.

3. From the thermal and kinetic data the energy difference between the (^5S) and the (^3P) state of the carbon atom is found to be 74 Cal. Both for the C—I linkage in ethylene iodide and for the energy difference between C—C and C=C a value of about 48 Cal. is obtained.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

PRECISION ACTINOMETRY WITH URANYL OXALATE

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For actinometry, uranyl sulfate with excess of oxalic acid has marked advantages, such as absence of dark reaction, great width of absorption band, zero order light reaction, a temperature coefficient of approximately unity, small effect of added electrolytes and finally the simplicity of the permanganate method of analysis. Boll[1] reported 50 molecules transformed per quantum at 254 mμ; Büchi[2] 1.07 between 400 and 470 mμ; Bowen and Watts[3] 1.0 at mean wave length 313 mμ; and Anderson and Robinson[4] 0.04 between 200 and 410 mμ. The system would doubtless be more useful to photochemists if the quantum yield were better known.

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[1] Boll, *Compt. rend.*, 156, 1891 (1913).

[2] Büchi, *Z. physik. Chem.*, 111, 269 (1924).

[3] Bowen and Watts, *J. Chem. Soc.*, 1607 (1926).

[4] Anderson and Robinson, THIS JOURNAL, 47, 718 (1925).

For three years we have critically studied this actinometer from radiometric and analytical standpoints, determining quantum yields at nine wave lengths from 494 to 254 mμ inclusive, with variation of concentrations, temperature and foreign electrolytes.

Materials.—To eliminate strongly absorbing impurities and those possibly catalytic, materials were carefully purified. Uranyl nitrate (P. W. R. "Analytical") was gently ignited in platinum, and the extract with 20% sulfuric acid evaporated until white fumes appeared. After several repetitions of this process a water extract[5] of the sulfate was evaporated, decanted, chilled and the crystals centrifuged and washed in platinum Gooch crucibles with protection against dust. Two more crystallizations, four washings and six centrifugings gave the final product, which was dried to incipient efflorescence over calcium chloride and preserved in stoppered vessels in a desiccator. Less than 0.01% of U^{++++} was detected by potassium permanganate. Oxalic acid (Mallinckrodt's "Reagent") was twice recrystallized, centrifuged and dried over calcium chloride. The composition of the uranyl sulfate was investigated in three ways. Direct ignition, corrected by Lundell and Knowles,[6] $HF-H_3BO_3$ method gave 69.41, 69.10 and 69.44% of UO_3. Precipitation as $(NH_4)_2U_2O_7$ followed by ignition according to Lundell gave 69.53, 69.36 and 69.51% of UO_3. The average value was 69.43 ± 0.05%. Sulfate, as $BaSO_4$, amounted to 19.62 ± 0.13%, *i. e.*, an excess of 0.20 ± 0.15% over the equivalent UO_3 as determined. Solutions were made up from conductivity water, filtered through sintered glass and kept in non-sol bottles covered with black enamel.

Apparatus.—The apparatus, kindly loaned by Dr. P. A. Leighton, was substantially as described previously.[7] We mention here only our most important refinements in construction and operation. We used his constant pressure lamp, also another constructed by us and operating under 800 mm., 175 volts and 3 amperes. Both lamps were rigidly mounted in a metal frame with leveling screws. A 5-kilowatt d. c. generator coupled to a synchronous motor proved to be a very constant source of current. Suitable inductance, resistance and an automatic circuit breaker were supplied. Much attention was given to controlling and recording small intensity variations. The monochromator now had a curved collimator slit whose image, at the exit slit, was rectilinear. At the latter, 19 mm. high, 750 ergs per sq. mm. per sec. was available at the most intense wave length, 366 mμ, and 15 at the weakest, 494 mμ, here used for the first time in quantitative photochemical work. Both slits were set at 0.75 mm. in Run 29; at 1.5 mm. in 1–5, 9–11, 16–17, 22–23, 38, 47, 49; at 2.8 mm. in 30–31, 48, 50–52; and at 1.0 mm. in all other runs. A large glass prism of extra dense flint, kindly loaned by the Rumford Fund, was substituted for quartz in Runs 30–31 and 50–52, and the results at 406 mμ so obtained were more heavily weighted owing to the improvement in resolution. The quartz cell, of trapezoidal cross section, was 2.65 cm. thick except in Runs 1–3, 9–11, 20, and 22–23, where $d = 3.06$ cm. All seams of the former cell had been fused by Schott and Gen. with minimal distortion of the faces. It had a cover with a

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[5] Meyer and Nachod, Ann., 440, 186 (1924).

[6] Lundell and Knowles, THIS JOURNAL, 47, 2637 (1925).

[7] P. A. Leighton and G. S. Forbes, *ibid.*, 51, 3549 (1929).

tubulure for a tiny screw stirrer projecting into the topmost (unilluminated) layer of solution; unstirred solutions showed about 10% less photolysis than stirred ones, owing to deposition of bubbles on the front window of the cell. The lateral faces were jacketed for circulation of water from a thermostat. Room temperature also was kept as near as possible to that of the cell. The thermopile-galvanometer system was first recalibrated against standards C-39 and C-40 from the Bureau of Standards, but as these deteriorated somewhat through use, final calibrations were based on a new standard, C-69. Dr. W. W. Coblentz kindly amplified the official directions in a personal conference with one of us. As the energy flux in our photolyses often exceeded that from the radiation standards under maximum load at 2 meters, the calibrations were extended to higher intensities by a method described elsewhere by one of us.[8] The reliability of these extrapolations was indicated by the fact that our absorption coefficients and quantum yields were identical at low and high intensities, respectively. For pile currents giving deflections in excess of 200 cm. (the length of scale used), auxiliary resistance patterns were calibrated with great care. Constant damping was obtained when the shunt resistance s and series resistance a were related to the pile resistance p thus: a $= p^2/(p + s)$. Under these conditions it was algebraically predicted that $\beta = 1 + p/s$ where β was the ratio of thermopile intensities with constant deflection referred to the standard circuit in which a $= 0$ and $s = \infty$. Experimentally this relation proved valid within 0.3%. This agreement proves the galvanometer alone responsible for the small decrease in sensitivity with increasing deflection.

The total energy flux emerging from the rear of the liquid-filled cell was measured by horizontal integration as described by Villars,[9] excepting that the beam was adjusted in height not to exceed that of the vertical row of junctions. Under these conditions it was shown by P. A. Leighton and Forbes[7] that the total energy flux was quantitatively obtained as $2\Sigma(B_1 + B_2 + \ldots)$ where B_1, B_2, etc., are energy readings with the pile at positions 1, 2, etc., spaced at 2-mm. horizontal intervals and sufficient in number to accommodate the whole beam. Use of slit widths = 1 mm. in several experiments necessitated 1-mm. spacing of thermopile observations in which cases the total energy flux = 1 X ZB. Each value of B is calculated from six to twelve galvanometer swings converted into ergs per sec. per mm. of beam width.

Horizontal integrations of relative intensity, ΣF, carried out in the same manner as above, but with the cell removed, were made before and after B integrations and at one to two hour intervals through long exposures (*cf.* Table II).

As the diverging light fell obliquely upon the junctions, the variation in deflection with departure from normal incidence was determined with parallel rays from a constant source. Each B value for a typical monochromatic beam was then corrected according to the angle of incidence and a correction averaging +0.7% thus found was applied to all ZB integrations.

The intensity of the diverging beam varies in a vertical as well as horizontal direction. We next tested the assumption made previously that the

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[8] Forbes, J. Phys. *Chem.*, 32, 490 (1925).

[9] Villars, THIS JOURNAL, 49, 326 (1927).

linear thermopile is capable of correctly integrating in the vertical sense. A horizontal slit of constant width was moved in definite steps from the bottom to the top of the thermopile, using a constant light flux of uniform distribution, and the local sensitivity factors were determined for each position. The same process was repeated in a beam of purposely exaggerated non-uniform distribution, and the above factors applied. The summation of corrected readings now agreed with the uncorrected sum within a few tenths of a per cent. A further experiment showed that with a quarter of the slit left unilluminated at each end, the direct reading was correct within 0.3%. This outcome convinced us that our method of horizontal integration was unaffected by non-uniformity of energy distribution, within such a limit of error.

The sensitivity of the thermopile–galvanometer system, which seemed to vary with room temperature, was frequently checked against a well-seasoned, calibrated lamp and small corrections applied as needed.

Reflection factors for the interfaces actually used were experimentally determined at each wave length and in addition the absorption coefficient of water was redetermined at 254, 265 and 313 mμ. The results agreed closely with Kreusler's figures.[10]

Photochemical Products.—These have been repeatedly studied both for oxalic acid alone and for oxalic acid sensitized by uranyl sulfate. Büchi,[2] whose findings appear the most satisfactory, concludes that in the latter case CO, CO_2, HCOOH and U^{++++} are the only products of importance. In our well-stirred solutions most of the carbon monoxide must have escaped during photolysis, and we also heated our solutions for ten to fifteen minutes at 80° in contact with air, which should have eliminated still more. Büchi holds that potassium permanganate attacks carbon monoxide along with oxalate. We proved that solutions of uranyl sulfate and oxalic acid saturated with carbon monoxide at 760 mm. and 20° and then heated as in our regular analyses gave exactly the same titer as solutions to which no carbon monoxide had been added. As photolyses in a special cell gave identical results under carbon dioxide, under air and *in vacuo*, we did not exclude air in any of our operations. We proved by cold titration with potassium permanganate that none of our photolyzed solutions could have contained more than 10^{-7} mole of $U(SO_4)_2$, although increase in ratio $[UO_2SO_4]/[H_2C_2O_4]$ and more protracted illumination would have formed more of it. Finally we proved that solutions containing formic acid in the largest concentrations which could have been present gave, under our analytical conditions, results identical with solutions containing the same amount of oxalic acid without any formic acid.

Analytical Method.—The cell was weighed to the nearest milligram empty, then with 6.7 g. (5.2 g. in runs 1–3, 9–11, 20 and 22–23) of solution.

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[10] Kreusler, *Ann. Physik*, 6,421 (1901).

After exposure, the bulk of the contents was pipetted into a 15-cc. test-tube, with blackened sides, clamped between two similar tubes filled with uranyl sulfate in the same concentration and suspended in a beaker of water at 80°. The cell was rinsed with 1 cc. of 18 N sulfuric acid, which was transferred to the test-tube. From a small weight buret 0.2 N potassium permanganate standardized against sodium oxalate from the Bureau of Standards was slowly added with vigorous stirring almost to an end-point. At this acid concentration and temperature the uranyl salt seemed greatly to reduce the induction period without need for excess manganous sulfate which would have made the end-point more unstable.[11] The resulting liquid was transferred back to the cell and then back again to the test-tube, so that rinsing of cell and pipet was accomplished without further dilution of the analysis—a very important point. Prom a second weight buret enough 0.01 N potassium permanganate was next added to give the faintest pink observable for thirty seconds while looking down on a white card through 10 cm. of solution. A weighed quantity of the original solution, which had been kept in the dark, was titrated under the same conditions (usually at the same time). Analyses appeared reproducible within 5×10^{-7} equivalent of potassium permanganate, **i. *e.*,** 0.1% of the sample, but as only 5% was photoly-zed the error in the latter quantity became 2%, **i. *e.*,** practically the same as the apparent radiometric error. We think it unlikely that any systematic errors of similar magnitude remained undetected.

Corrections and Computations.—Intensity summations, ΣB behind the cell and ΣF with cell removed, were described above. The sequence of observations is illustrated in the sample calculation (Table II). Where ΣF_{H_2O} is interpolated from the nearest ZF integrations to correspond chronologically to ΣB_{H_2O}, the summation behind the cell filled with water, their ratio

$$K = \Sigma F_{H_2O} / \Sigma B_{H_2O} \qquad (1)$$

is independent of drift in intensity. K was determined at the beginning and end of each experiment, with the same cell used for the photolysis, and the average used to interpolate ΣB_{H_2O} to any time t for which ΣF_t is the corresponding direct reading, thus $(\Sigma B_{H_2O})_t = \Sigma F_t/K$. The incident intensity in total ergs per sec., I_0, at time t is then

$$(I_0)_t = 2\,(\Sigma B_{H_2O})_t \times R = 2\,\frac{\Sigma F_t}{K} \times R \qquad (2)$$

where

$$R = \frac{1 - 0.085}{1 - r_p} \times \frac{1}{1 - r} \cdot \frac{1}{10^{-wd}} \qquad (3)$$

The observed transmission by the crystalline quartz pile window at an experimental wave length is denoted by $(1 - r_p)$, while $(1 - 0.085)$ is its

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[11] **Compare** Bobtelsky and Kaplan, *Z.* anorg. *allgem. Chem.*, 172, 196 (1928).

average transmission in radiation from the standard lamps, as given by Coblentz. (1 – r) is the observed transmission of the rear window of the cell when filled with water; (w) is the observed absorption coefficient of water (log base 10) and d the thickness of layer in cm. R thus reduces $2\Sigma B_{H_2O}$ to absolute ergs per second incident on the front of water, also solution layer (factor 2 applies where interval between B_1, B_2, etc., is 2 mm., as previously pointed out). Table I summarizes numerous experimental determinations during this research.

TABLE I

EXPERIMENTAL OBSERVATIONS

Wave length	$1-r_p$	$1-r$	W	R
2000	(0 915)	. .	. .	. . .
435	.909	0.94	. .	1.074
366	.905	.94	. .	1.078
313	.897	.938	. .	1.087
265	.885	.934	0.008	1.16
254	.880	.933	.012	1 21

A cell with crystal quartz rear window and d = 3.06 cm. was used in this case; a fused quartz cell, d = 2.65 cm., in all other cases. 0.915 is the transmission of crystal quartz at 2μ according to Coblentz, Observation on a second window, d = 0.5 mm., with the pile window in place gave nearly this figure. Beckman and Dickinson[12] found 0.906 for a crystal quartz window (no thickness given).

The transmissions observed above are lower than predicted by Fresnel's equation, probably due to surface imperfections and impurities in the quartz. Thus at 254 mμ and 435 mμ the ideal values of R are 1.19 and 1.05, respectively. Kreusler's values[10] for w are 0.010 and 0.012 at 265 and 254 mμ, respectively.

If I is the total intensity, in ergs per sec., reaching the rear of the solution layer, the transmission may be shown to be

$$\frac{I}{I_0} = \frac{\Sigma B_{\text{soln.}}}{\Sigma F_{\text{soln.}}} \times K \times 10^{-wd} \tag{4}$$

For all cases where absorption by water is negligible, 10^{-wd} approaches unity.

Where $(I_0)_1$, $(I_1)_2$, etc., are the incident intensities at the mid-times of the exposures Δt_1, Δt_2, etc. (sec.), respectively, the total energy E_0 in ergs incident on the solution during the whole photolysis is

$$E_0 = (I_0\Delta t)_1 + (I_0\Delta t)_2 + \ldots \tag{5}$$

$$= \frac{2R\Sigma(\Delta t\Sigma F)}{K} \tag{5a}$$

As $1 - (I/I_0)$ = fraction absorbed during the first passage of the light and rI/I_0 is reflected back to contribute $(1 - (I/I_0))rI/I_0$ to the gross fraction absorbed, the total ergs A absorbed during a photolysis follows as

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[12] Beckman and Dickinson, THIS JOURNAL, 52, 126 (1930).

$$A = E_0\left(1 + \frac{rI}{I_0}\right)\left(1 - \frac{I}{I_0}\right) \tag{6}$$

Equation 6 becomes $A = E_0$ when $I/I_0 \rightarrow 0$. As this happened to be the case at all wave lengths where absorption by water was appreciable, in practice Equation 4 became $I/I_0 = (\Sigma B_{\text{soln.}}/\Sigma F_{\text{soln.}})K$. Over the range of decomposition in our experiments, I/I_0 remained unchanged, as is illustrated in Table II. Otherwise it would be necessary to calculate A as $A_1 + A_2 + \ldots$ for the several exposure periods, separately reckoned.

Finally, q, the total quanta absorbed by the solution, follows from

$$q = \frac{A}{h\nu} \tag{7}$$

where $h = 6.554 \times 10^{-27}$ and $\nu = 3 \times 10^{10}/\lambda_{\text{cm.}}$

By the analytical procedure already described, m, the moles of oxalic acid decomposed, was determined and the gross yield ϕ in molecules decomposed per quantum absorbed was calculated

$$\phi = 6.063 \times 10^{23}\,\frac{m}{q} \tag{8}$$

Illustration of Calculations.—Run 27, Table IV, was chosen to illustrate the usefulness of ΣF integrations in compensating for variation in intensity much greater than was characteristic of our experiments. In this connection, note particularly the agreement in K values and also I/I_0 values at the beginning and end of the run.

TABLE II

METHOD OF ENERGY OBSERVATION AND CALCULATION

Run 27; 0.01 M UO_2SO_4, 0.05 M $H_2C_2O_4$ at 366 mμ and 25°. Cell is of fused quartz, $d = 2.65$ cm., $R = 1.078$

Observation	Av time from start	Δt sec.	ΣF ergs/sec.	ΣB ergs/sec.	Calculations
ΣF	0 mins.		8850		
ΣB_{H_2O}	4		(8755)	6740	$K = 1.30$ (Eq. 1)
ΣF	26		8275		
$\Sigma B_{\text{soln.}}$	36	*	(8285)	2150	$I/I_0 = 0.338$ (Eq. 4)
ΣF	40		8290		
Ex. 1	92	5040	(8020)		$\Delta t \Sigma F = 4.05 \times 10^7$
ΣF	164		7660		
Ex. 2	209	5220	(7620)		$\Delta t \Sigma F = 3.98 \times 10^7$
ΣF	260		7580		
Ex. 3	303	4920	(7550)		$\Delta t \Sigma F = 3.71 = 10^7$
ΣF	352		7505		
$\Sigma B_{\text{soln.}}$	368	*	(7470)	1930	$I/I_0 = 0.337$
ΣF	404		7400		
ΣB_{H_2O}	411		(7370)	5635	$K = 1.31$
ΣF	420		7360		

$\Sigma(\Delta t \Sigma F) = 11.75 \times 10^7$ ergs

$E_0 = 19.4 \times 10^7$ ergs (Eq. 5a)

$A = 13.1 \times 10^7$ ergs (Eq. 3)

$q = 24.4 \times 10^{18}$ quanta (Eq. 7)

(1) Times of exposure (*) during observations of $\Sigma B_{\text{soln.}}$ were included in Δt_1 and Δt_3, respectively, as they were only of the order of 150 sec. (2) ΣF values in parentheses were interpolated to the times indicated. (3) Av. $K = 1.305$; av. $I/I_0 = 0.3375$.

TABLE III

ANALYTICAL DATA FOR ABOVE RUN 27

[UO_2SO_4], moles per kg., 0.00990

[$H_2C_2O_4$], moles per kg., original, 0.04980

Wt. soln. used, 6.748 g.

Wt. $KMnO_4$ [0.2180 N], required (after), 2 887

Moles decomp. $= (1/1000)\ (6.748 \times 0.04980 - (0.2180 \times 2.887)/2)$

$= 0.0214 \times 10^{-3}$

Molecules decomp. $= (0.0214 \times 10^{-3}) \times 6.063 \times 10^{23} = 12.95 \times 10^{18}$

From Table II, $q = 24.4 \times 10^{18}$ and $\phi = \mathbf{0.53}$

The summary of our data is given in Tables IV–VI.

TABLE IV

A. RESULTS AT 25° WITH 0.01 M UO_2SO_4 + 0.05 M $H_2C_2O_4$ (CONTINUOUS STIRRING)

	λ, mμ	Moles per kg. UO_2SO_4	Moles per kg. $H_2C_2O_4$	Decomp., %	I/I_1	Av. I_0 ergs/sec.	Quanta absorbed × 10^{-18}	Molecules decomp. × 10^{-18}	Yield, ϕ
1	255	0.00997	0.05050	3.1	0.000	1625	7.85	4.95	0.63
2		.00997	.05045	4.1		1955	11.00	6.35	.58
									.602
3	265	,00997	,05045	5.7	.000	3090	15.30	8.85	.58
4		.00997	,05043	4.1		2550	13.90	7.88	.565
5		,00997	,05040	3.9		2200	12.20	7.33	.60
									.582
6	300	,0100	.04980	2.4	,000	2570	7.95	4.67	.59
7		.00991	,05041	2.1		2910	6.80	3.88	.57
8		.00991	.05027	4.7		4500	16.70	9.32	.56
									.570
9	313	,00997	.05040	5.0	.000	3905	14.85	8.06	.545
10		.00997	.05040	10.4		5580	31.20	16.60	.53
11		,00997	.05040	12.0		4955	33.70	19.20	.57
12		,00997	.05040	7.5		3865	23.90	14.20	.595
13		,00997	.05040	8.5		5440	28.50	16.20	.57
									.561
14	366	.00997	.05040	4.8	,336	7220	19.20	9.95	.52
15		.00997	.05040	5.4	.330	7945	22.65	11.20	.495
16		,00997	.05040	4.1	,330	4290	18.80	8.61	.46
17		,00997	.05040	4.5	.329	3825	18.35	9.34	.51
18		.00991	.04998	4.8	.333	5390	21.35	9.80	.46
19		.00991	.04998	6.0	.328	4830	24.25	12.30	.505
20		.00991	,04998	7.3	.277	5350	25.50	12.45	.49
21		.00991	.04998	4.0	.330	9140	18.30	8.10	.445
22		.00991	.05019	15.8	.277	17500	56.45	27.60	.49
23		.00991	.05019	3.8	.279	16590	14.60	6.60	.45
24		.00991	.05041	1.9	.330	6100	7.20	3.46	.48
25		.01 ±	.05027	5.4	.290	14350	20.40	10.80	.53
26		.01 ±	.05027	4.7	.294	14300	20.05	9.80	.50
27		.01000	.04980	6.4	.338	12760	24.40	12.95	.53
									.492

TABLE IV (Concluded)

	λ, mμ	Moles per kg. UO_2SO_4	Moles per kg. $H_2C_2O_4$	Decomp., %	I/I_1	Av. I_0, ergs/sec.	Quanta absorbed $\times 10^{-18}$	Molecules decomp $\times 10^{-18}$	Yield, ϕ
28	406	0 00991	0.05020	3 9	0 413	3960	15 45	8 04	0.52
29		.00991	.05021	1.7	.418	1600	6 80	3 52	52
30		.01000	.04980	5 1	.418	9125	18.35	10 25	.56
31		.01000	.04980	3 4	426	7715	12.20	6 95	.57
									.563
32	435	,00991	.05019	4 6	.474	4825	15 50	9 46	.61
33		.00991	.05019	5 1	.482	5550	18 85	10 50	.555
34		.00991	.05019	5 8	.483	5380	20 50	12 00	.585
									.584

The italicized figures are weighted average values of ϕ for the wave lengths in question.

TABLE V

RESULTS AT 9.8° WITH 0.01 M UO_2SO_4 + 0.05 M $H_2C_2O_4$ (CONTINUOUS STIRRING)

	λ, mμ	Moles per kg. UO_2SO_4	Moles per kg. $H_2C_2O_4$	Decomp., %	I/I_0	Incident ergs/sec. I_0	Quanta absorbed $\times 10^{-18}$	Molecules decomp. $\times 10^{-18}$	Yield ϕ
35	313	0.00997	0 05040	7.3	0 000	4085	26.75	13 90	0 520
36		.00997	.05040	6.7		3530	23.15	12 80	.550
37		.00997	.05040	5.6		3080	20.05	10 80	.540
									.536
38	366	.00997	.05040	6 0	.382	9015	27.30	12 50	.460
39		.00997	.05040	6 5	.388	6365	27.50	13 50	.490
40		,00997	.05040	6 0	.387	6655	27.70	12 45	.450
41		.00991	.04998	3 8	.395	4425	16 30	8 00	.490
									.471

TABLE VI

RESULTS AT 25° WITH VARIOUS MIXTURES (CONTINUOUS STIRRING)

	λ, mμ	Moles per kg. UO_2SO_4	Moles per kg. $H_2C_2O_4$	Decomp., %	I/I_0	Incident ergs/sec. I_0	Quanta absorbed X 10^{-18}	Molecules decomp X 10^{-18}	Yield, ϕ
42	313	0.00100	0.05044	2.5	0.056	3185	9 20	5.05	0.550
43		.00100	.05044	3.4		3055	11 40	6 90	.605
44		.00100	.05044	3.4		5090	12.00	6.95	.580
									.580
45	313	.0100	.01002	6.1	.000	2900	5.05	2 50	.49
46		.0100	.01002	8.5		2710	6.40	3.45	.54
									.52
47	313	.0200	.03954	5 1	.000	23430	14.75	8 20	.555
48	366	,0200	.03954	7.0	.142	29610	24 00	11.20	.465
49	435	.0200	.03932	8.8	.251	6910	27.00	14 20	.525
50		.0200	.03911	19.6	.274	19420	59 30	31 60	.535
									.532
51	460–480	.0200	.03911	0 6	.673	780	2 25	0.90	.40
52	494	.0200	.03932	(−0.08)	,935	740	0.55	(−010)	.00
53	366	.0100	.04997	7 9	.311	12270	34 15	15 95	.465
54	366	.0100	.04976	5.9	,364	11690	25.60	11.75	.460
55	366	.0100	.04999	5 6	.324	10410	24.60	11.50	.465

The solution of Run 53 was 0.02 M in NaOH, that of Run 54 was 0.04 *M* in H_2SO_4 and that of Run 55 was 0.04 M in Na_2SO_4.

Tables IV–VI and also Fig. 1 give gross quantum yields without correction for light absorbed by oxalic acid and water, Quantum yields and theoretical conclusions for other photolyses which have been based on $\phi = 1$ for uranyl oxalate will now require revision. We have proved that the reciprocity law holds within a few per cent. at least over a four-fold range of intensity at 366 mμ. An unmistakable minimum in ϕ occurs at this wave length where the threshold of the ultraviolet absorption band meets the end of visible absorption band. Beyond **435** mμ, ϕ decreases **rapidly** with frequency. Absorption is increased by sodium sulfate or

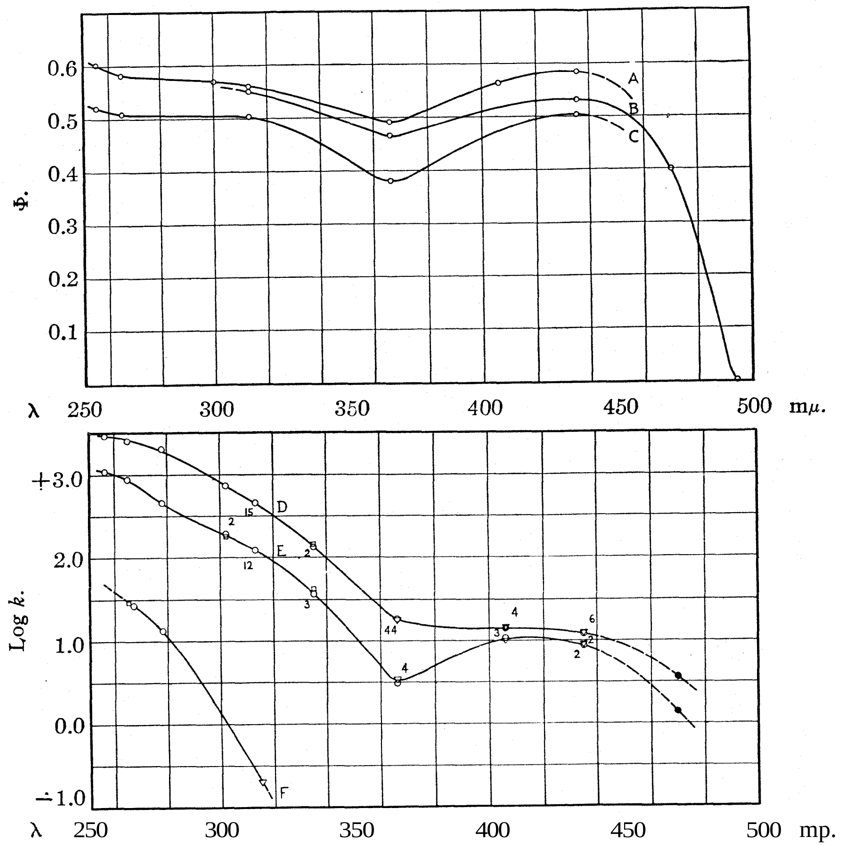

Fig. 1.—Above, gross quantum yield at 25° plotted against wave length. Curve A summarizes Table IV; Curve B same solution unstirred; Curve C, a stirred solution 0.02 M in UO_2SO_4 and 0.04 M in $H_2C_2O_4$.

Below, absorption coefficients at 25° plotted against wave length. Curve E for 0.01 M UO_2SO_4; Curve F for 0.05 M $H_2C_2O_4$; Curve D for a solution 0.01 M in UO_2SO_4 and 0.05 M in $H_2C_2O_4$. Points designated ○ and A by spectroradiometry, ☐ by photographic photometry, ● chiefly by a Keuffel and Esser visual spectrophotometer.

sodium hydroxide, but is decreased by sulfuric acid. All three, especially the last two, cut down ϕ. Variations in [UO_2SO_4] have little effect, provided that [$H_2C_2O_4$]/[UO_2SO_4] >5. As this ratio is diminished, + falls off also, as Büchi[2] first proved. We have recalculated ϕ (Table VII) at **313** my by apportioning the absorbed light, A, between the compound c, of UO_2SO_4 and $H_2C_2O_4$ (*i.e.*, $UO_2HC_2O_4^+$ or $UO_2C_2O_4$?) and u, the uncombined uranyl sulfate, assuming that c has the maximal absorption coefficient attainable with excess oxalic acid after correction for the small absorption by this excess of oxalic acid.

TABLE VII

GROSS AND NET QUANTUM YIELDS

(U^{VI}) total	($H_2C_2O_4$) total	A_u	A_c	ϕ_{gross}	ϕ_u	ϕ_c
0.001	0.050	0.008	0.976	0.58	70	0.59
.010	.050	.011	.987	.56	51	.57
.020	.040	.020	.978	.56	27	.57
.010	.010	.115	.885	.52	4.5	.59

The greater consistency of the net ϕ_c as compared with that of ϕ_{gross} harmonizes with the views of Büchi,[2] also quoted by Pierce,[13] to the effect that uranyl sulfate and oxalic acid in equal moles form the photolyte. This might be a definite chemical compound such as $UO_2HC_2O_4^+$ or $UO_2C_2O_4$, or an equivalent optical cluster according to Weigert.[14] On the other hand, if one assumes, with Müller,[15] that excited UO_2^{++} decomposes oxalic acid through a collision of the second kind, then ϕ_u, based upon uncombined uranyl sulfate, becomes highly variable and improbably large. Müller proves that Cl′, Br', CNS′ and I inhibit the photolysis in the order given, and attributes this effect to an increasing efficiency in deactivating excited UO_2^{++}. These ions, of course, might as well deactivate excited $UO_2HC_2O_4^+$, $UO_2C_2O_4$ or optical cluster. The complex-forming tendency of these ions, also, generally increases in the order given, which suggests an increasingly effective competition against C_2O_4'' for union with UO_2^{++}. Such an outcome would readily explain why I is the most effective inhibitor, without prejudice to the views of Biichi.

Temperature Coefficient.—Quantum yields at **366** mμ and at **313** mμ were compared at **25.0** and at **9.8'**. The experiments at **9.8'** were carried out in winter with a room temperature of 8°—an important precaution. The sensitivity of the radiometric system appeared 6% higher at 8° than at 25°.

It will be noted that if the absorption at 25° had been used to calculate ϕ at 9.8° and 366 my, the temperature coefficient would have come out **1.14** instead of **1.03.** Neglect of this precaution has vitiated many published temperature coefficients.

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[13] Pierce, THIS JOURNAL, **51, 2731 (1929).**

[14] Weigert, *Z. physik. Chem.*, **102,416 (1922); 106,426 (1923).**

[15] Müller, *Proc. Roy. Soc.* (London), **A121,** 315 **(1928).**

TABLE VIII

λ	t, °C.	Σkc	$\phi_{av.}$	$\phi_{(t+10)}/\phi_t$	$\Sigma kc_{(t+10)}/\Sigma kc_t$
366	**25.0**	**0.1822**	**0.492**		
366	**9.8**	.156	.471	**1.03 ± 0.025**	**1.11**
313	**25.0**	**Absorption**	.561		
313	**9.8**	**complete**	.536	**1.03 ± 0.025**	..

Actinometry in Monochromatic Light, X $<$ 500 mμ.—The data given above can be utilized to measure (a) radiant flux, (b) quantum yields, (c) moles transformed in other photolytes and (d) adsorptions. The actinometer solution must be 0.0100 M in uranyl sulfate and 0.050 M in oxalic acid, all solutions must be stirred (temperature is roughly 25°), and our analytical method closely followed,

(a) Set a cylinder or rectangular prism of actinometer solution with its front window (quartz if $\lambda < 366$ mμ) perpendicular to the L_0 beam. If absorption is complete, $L_0 = 6.06 \times 10^{23}\ m/\Delta t\phi$ where L_0 gives average quanta per sec. over the interface L_0 between front window and solution ($L_0 \times 1.05$ at the air interface of front window) and m is the moles of oxalate decomposed in At seconds. ϕ is interpolated from the average ϕ in Table III. Analytical errors have perhaps the smallest effect when d, the thickness of the layer, is about 2 to 3 cm. If X $\geqq$ 366 mp, the absorption is not "complete," and L_0 as found above must be multiplied by $(1–10^{-kd})$, where k is the antilog of the proper ordinate of Curve D in Fig. 1. The solution in a thickness of 2.5 cm. transmits 0.00, 0.35, 0.43, 0.50 and 0.83 of L_0 at 313, 366,406,435 and 470 mμ, respectively. If $(1–10^{-kd}) < 0.90$, the rear window should be painted black to minimize backward reflection.

(b) An "unknown" aqueous system simultaneously illuminated in a similar vessel in an equivalent position (or subsequently in the actinometer vessel if the light source is constant) will, if absorption is complete, likewise consume L_0 quanta per second, so that $\phi' m \Delta t' = \phi m' \Delta t$. If the second system does not absorb completely, $(1–10^{-k'c'd})$ must be measured by spectrophotometer or calculated from published data on absorptions or determined as suggested under (c). If it contains also an inert absorbent, the light absorbed must be properly apportioned. If a gas is investigated, additional corrections for reflection factors must be included in careful work.

(c) After ϕ' is known, m" may be predicted for any other time under these identical conditions. We suggest a compound actinometer (Fig. 2) to evaluate relative quantum yields and even absorptions in terms of analytical results exclusively. Reflection corrections are small if the rear window is painted black. The four cells are identical in dimensions and I refers to the relative intensity of parallel monochromatic light at the point designated. If Cells 1 and 2 are filled with actinometer solution, and 3 and 4 with the "unknown" system, also m_1, m_2, m_3, m_4 are the respective moles transformed (m_3 and m_4 already corrected for any dark reaction) then $\phi' = \phi \left(\frac{m_3}{m_1}\right)^2 \left(\frac{m_1 - m_2}{m_3 - m_4}\right)$ which becomes $\phi' = \phi \frac{m_3}{m_1}$ for complete absorption in Cells 1 and 3. If actinometer solution is placed in Cells 1, 2 and 4 and "unknown" in 3, $\phi' = \phi \frac{m_3}{m_1}\left(\frac{m_1 - m_2}{m_1 - m_4}\right)$.

(d) If the four cells are filled as first indicated, the relative absorptions can be found. The transmission of the actinometer solution $I_1/I_0 = I_2/I_1 = m_2/m_1$ and that of the "unknown" $I_3/I_0 = I_4/I_3 = m_4/m_3$. The errors are magnified, in the calculation, if the absorptions are very strong or very weak.

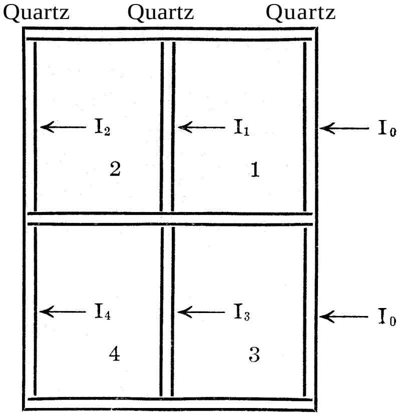

Fig. 2.—Compound Actinometer.

Polychromatic Light.—If the spectral energy distribution of the source is unknown but constant, average quantum yields are found as in (b) by using only that portion of the spectrum which is completely absorbed by both solutions. The procedure described in the first sentence of (c) is still valid even for variable time and total intensity. It must be remembered that the spectral energy distribution of sunlight is highly variable. If preliminary experiments with various filters prove that the photochemical absorption curves of actinometer and of the "unknown" are both "cut off" within about the same wave length range, and if it is certain that the absorption spectrum of the "unknown" has no "holes," procedure (c) is fairly safe even if both solutions transmit a good deal of active light. The tacit assumption remains that ϕ'/ϕ is nearly independent of wave length. The mercury arc serves well in the above cases, for its spectrum so far as our actinometer and many other photosensitive systems are concerned terminates at 435 mμ where quantum yields and absorptions are still considerable. Thermal radiators, however, emit an excessive proportion of light in the blue-green and green, where neither the respective absorptions nor quantum yields could be expected to correspond.

Our actinometer solution could be advantageously used in the self-integrating actinometer described by Dorcas and Forbes,[14] instead of benzoquinone in 50% alcohol. As $\phi_{\text{quinone}}/\phi$ is nearly constant over the "erythema range" the same light filter would suffice. Many other photochemical reactions could be studied in polychromatic light using our actinometer solution and data if proper filters were developed.

We gratefully acknowledge an appropriation from the Milton Fund to defray the expenses of this research and the loan of a motor generator set

[14] Dorcas and Forbes, THIS JOURNAL, 49, 3081 (1927).

by the General Electric Company used in the earlier experiments. During the last year of the work the first-named author held the du Pont Fellowship of the Division of Chemistry.

Summary

The photolysis of certain uranyl oxalate solutions in nine approximately monochromatic radiations has been reinvestigated with elaborate (and in some cases novel) radiometric and analytical precautions.

The gross quantum yield ϕ at 25° for a solution **0.01** M in uranyl sulfate and **0.05** M in oxalic acid varies between **0.60** at **254** mμ to **0.58** at **435** mμ with a minimum of **0.49** at **366** mμ. These values are about half those generally in use at the present time.

ϕ is diminished by sodium sulfate, by sodium hydroxide and by sulfuric acid, in spite of the fact that the first two enhance total absorption.

The temperature coefficient, ϕ_{t+10}/ϕ_t, is $1.03 + 0.035$, between **10** and 25°, both at **366** mμ and **313** mμ.

If the light presumably absorbed by uncombined uranyl sulfate is subtracted before calculating ϕ for solutions containing no great excess of oxalic acid, ϕ becomes nearly independent of their concentrations.

These calculations give some support to the view that the photolyte is $UO_2HC_2O_4^+$ or $UO_2C_2O_4$ or some optical cluster equivalent to one of these and make it seem somewhat improbable that the photolysis depends mainly upon collisions of the second kind between excited UO_2^{++} and $H_2C_2O_4$.

Detailed suggestions for actinometry in monochromatic and in polychromatic light are offered. The limitations of the latter procedure are emphasized.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 4]

THE DISSOCIATION OF CARBON DIOXIDE IN THE ELECTRODELESS DISCHARGE

BY HERSCHEL HUNT WITH WALTER C. SCHUMB

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The dissociation of carbon dioxide by the application of other than thermal energy has been studied by a number of investigators. Thus Lefebvre and Montagne[1] found that in the electric arc the dissociation proceeds in perfect accord with the prediction based upon the thermal decomposition of carbon dioxide. Carbon monoxide was unchanged when traversed by the arc or spark discharge.

Lind,[2] using alpha particles, has shown that oxygen forms O_2^- and

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[1] Lefebvre and Montagne, *Bull. soc. encour. ind. nat.*, 127,917 (1928).

[2] Lind, *Trans. Am. Electrochem. Soc.*, **44**, 66 (1923).

thereby chemical action with carbon monoxide is promoted. Neither carbon dioxide nor carbon monoxide can accept the electron.

Busse and Daniels[3] found no relation to exist between amount of decomposition of gases, such as nitric oxide and carbon dioxide, and the heats of formation or free energies of the gases. They found that cathode rays gave the same comparative results as alpha particles, and concluded that actual decomposition was brought about by the free electron.

The present investigation was undertaken with the object of observing the influence of the electrodeless discharge upon the decomposition and the synthesis of carbon dioxide. It constitutes an extension of the work described in another article upon the dissociation of ammonia.[4]

It is not proposed in this paper to offer a complete interpretation of the phenomena observed, because at the present writing such an explanation would be largely conjectural. The experimental facts, however, we believe merit setting forth, the theoretical significance of these facts being left for subsequent clarification.

Procedure

The apparatus employed in the earlier study has been greatly improved, and is shown diagrammatically in Fig. 1. We are indebted to Professor V. Bush of this Institute for the suggested arrangement. The wave length of the set as shown was found to be 34 meters, corresponding to a frequency of 8820 kc.

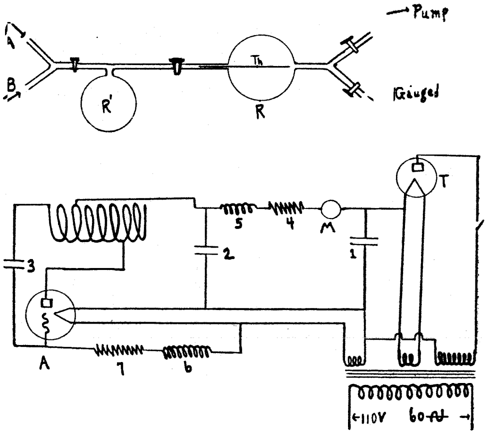

Fig. 1.—T, UX 866 mercury rectifying tube; M, 110-ma. milliammeter; A, UV 203 A power transformer tube, 50-watt; 1, 2-mfd. 1500-v. fixed condenser; 2, 0.002-mfd., 5000-v. fixed condenser; 3, 0.0005-mfd. 5000-v. fixed condenser; 4 and 7, 5000-ohm, 50-watt resistances; 5 and 6, radio frequency chokes (4" X 5/8", No. 22 wire).

The transformer operated on a 110-v. 60-cycle circuit and supplied T with 2.5-v. filament current, A with 10 v., and T with 825 v. at 150 ma., d. c. half-wave current. The solenoid, 10 inches in diameter, was made of flat copper strip 1 cm. in width. When tapped as shown the wave length produced was 34 m. Higher wave lengths were obtained by increasing the number of turns tapped off on the solenoid.

The reaction system, shown in Fig. 1, consisted of R, a one-liter pyrex bulb in which was placed a thermometer, Th, and R', a reservoir in which gases were mixed before using. To A and B were connected purification and drying trains for the entering gases. Gas mixtures were made up by controlling the individual partial pressures, using a

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[3] Busse and Daniels, THIS JOURNAL, 50, 3271 (1928).

[4] Schumb and Hunt, *J. Phys. Chem.*, 34, 1919 (1930).

manometer in conjunction with the McLeod gage. R was thoroughly evacuated and swept out several times with the gas mixture. Then a sample was drawn from R′ into R and the pressure lowered to the desired value; pressure and temperature readings were taken and the discharge started. After the passage of the discharge (regularly an interval of five minutes) the bulb, R, was allowed to come to the original temperature, which process required over one hour, and the final pressure was then taken at the original temperature. Since the room temperature did not vary over 0.1° in the course of any experiment, and since the gas was always measured at the same temperature, we may assume our measurements to be accurate to within 0.2%.

The carbon dioxide was generated by heating pure sodium bicarbonate. It was carefully dried by passage through phosphorus pentoxide. The carbon monoxide was made from concd. formic acid and concd. sulfuric acid. Most of the water vapor left in the gas was condensed by strong chilling in a gas trap. Traces of carbon dioxide were then removed by passing through solid caustic potash, and the gas was finally thoroughly dried by phosphorus pentoxide. Commercial compressed oxygen was passed over potassium hydroxide and phosphorus pentoxide before use.

In Table I typical data are given for the decomposition of pure carbon dioxide at pressures ranging from 0.25 to 2.82 mm. The first two columns show, respectively, the initial and final pressures, the third column gives the calculated percentage decomposition on the basis of the relationship

$$D = \frac{2(p_f - p_i)(100)}{p_i}$$

and the last column gives the corresponding value of K_p, the equilibrium constant, calculated according to the equation

$$K_p = \frac{(py^3/2)^{1/2}}{(1-y)(1+y/2)^{1/2}}$$

These results are shown graphically in Fig. 2, Curve I, wherein the percentage decomposition is plotted against the equilibrium pressure.

TABLE I

EXPERIMENTAL RESULTS

P_i, (mm.)	P_f, (mm.)	D, (%)	K_p	P_i, (mm.)	P, (mm.)	D, (%)	K_p
0.25	0.375	100.0	...	0.82	1.00	43.9	0.3320
.27	.40	96.3	9.375	0.925	1.105	38.9	.2708
.28	.41	92.86	4.690	1.06	1.25	35.85	.2436
.33	.47	84.8	2.087	1.175	1.36	31.5	.1978
.34	.48	82.35	1.739	1.36	1.555	28.68	.1776
.39	.54	76.9	1.289	1.61	1.81	24.8	.1390
.45	.60	66.67	0.7755	1.73	1.94	24.3	.1389
.495	.65	62.6	.6581	2.16	2.40	22.2	.1397
.56	.72	57.1	.5319	2.72	3.01	21.3	.1457
.67	.84	50.75	.4259	2.82	3.11	20.6	.1398
.76	.935	46.05	.3562				

Qualitatively the presence of carbon monoxide in the resulting gas after the passage of the discharge was confirmed by the blackening of palladious chloride paper, and sufficient oxygen was produced to cause a darkening of fresh alkaline pyrogallol solution.

Since the carbon dioxide is not completely decomposed at pressures greater than 0.25 mm., it is evident that an equilibrium is reached. That such is the case was definitely proved by the synthesis of the gas from a mixture of carbon monoxide and oxygen. The data obtained, using a mixture of two volumes of carbon monoxide and one volume of oxygen, are given in Table II.

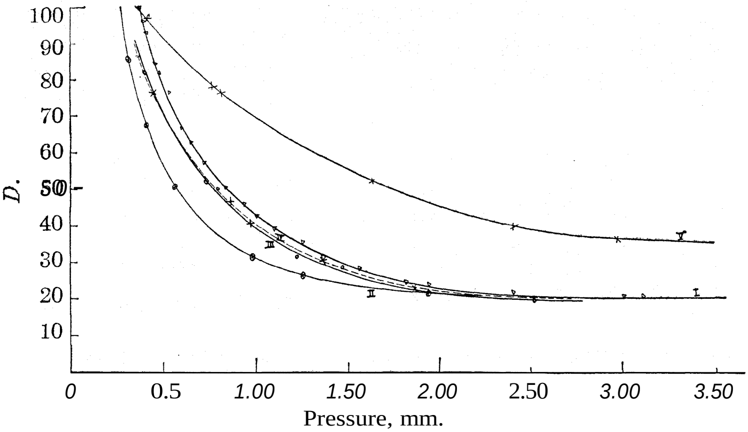

Fig. 2.—I, Decomposition of CO_2; II, synthesis: $CO/O_2 = 2$; III, decomposition: $CO_2/CO = 1$; IV, decomposition: $CO_2/O_2 = 1$; V, decomposition: $CO_2/He = 1$.

TABLE II

DATA OBTAINED

P_i	P_f	S	K_p
0.33	0.315	13.64	1.907
.46	.41	32.7	0.6613
.67	.56	49.3	.3456
1.27	.98	68.5	.1679
1.65	1.25	72.7	.1531
2.62	1.94	77.89	.1247

The third column lists the percentage of carbon monoxide converted into carbon dioxide. These data are also represented in Fig. 2, Curve II. The discharge passed for five minutes in all cases. After the discharge the gas was tested for carbon dioxide by passage through clear barium hydroxide solution. A dense turbidity was produced. A blank test made on the mixture which had not been subjected to the discharge gave a negative result.

The effect of varying composition of the gas mixture was now studied. The proportions of oxygen and of carbon monoxide in the original gas mixtures were increased above the stoichiometrical requirements and in a third experiment carbon dioxide was diluted with 50% of helium to observe the effect of an inert gas. The helium was freed before use from carbon dioxide, oxygen and water vapor. The results of these experiments are shown in Table III. *S* is based in all cases upon the fraction of carbon monoxide changed to carbon dioxide.

TABLE III

A. SYNTHESIS OF CARBON DIOXIDE WITH EXCESS OXYGEN. VOL. RATIO $CO/O_2 = 1$

P_i	P_f	S	K_p
0.31	0.29	25.8	1.0567
.45	.415	31.11	0.9627
.62	.56	38.71	.7917
1.15	.99	55.65	.5134
1.57	1.30	68.88	.3254
2.42	1.95	77.68	.2472
2.87	2.26	85.02	.1601

B. SYNTHESIS OF CARBON DIOXIDE WITH EXCESS CARBON MONOXIDE. VOL. RATIO $CO/O_2 = 4$

0.51	0.48	14.7	1.557
.62	.57	20.16	1.078
.70	.63	25.0	0.7937
1.17	1.00	36.32	.4428
1.67	1.38	43.4	.2738
2.84	2.28	49.3	.0917

C. SYNTHESIS OF CARBON DIOXIDE IN PRESENCE OF HELIUM. VOL. RATIO $He/(2CO + O_2) = 1$

0.33	0.3275	4.5
0.72	0.69	25.0
1.15	1.08	36.52
2.22	1.995	60.8

D. DECOMPOSITION OF CARBON DIOXIDE IN PRESENCE OF OXYGEN. VOL. RATIO $CO_2/O_2 = 1$

P_i	P_f	D	K_p
0.38	0.4525	76.31	1.646
.77	.86	46.76	0.6054
.88	.97	40.91	.504
1.26	1.36	31.74	.3979
1.76	1.865	23.86	.311

E. DECOMPOSITION OF CARBON DIOXIDE IN PRESENCE OF CARBON MONOXIDE. VOL. RATIO $CO_2/CO = 1$

0.34	0.41	82.35	2.731
.65	.735	52.31	0.931
.71	.80	50.70	.9169
1.13	1.22	31.85	.5802
1.37	1.47	29.2	.5771
2.40	2.525	20.83	.5393

F. DECOMPOSITION OF CARBON DIOXIDE IN PRESENCE OF HELIUM. VOL. RATIO $He/CO_2 = 1$

0.33	0.41	96.96
.64	.765	78.12
.68	.81	76.47
1.44	1.63	52.78
2.23	2.45	39.46
2.72	2.97	36.77

Preliminary experiments employing pure oxygen at pressures ranging from 0.82 to 1.8 mm. gave no pressure change; proving that ozone was not formed under these conditions. The gas gave a pale yellow glow which filled the bulb completely without the appearance of banding as in most of the other cases studied. Carbon monoxide alone gave no pressure changes when subjected to the discharge.

The passage of the discharge was in all cases accompanied by a rise in temperature, which, in a five-minute interval, amounted to about 20°. For this reason the 0.1° thermometer was enclosed in the bulb, as shown in Fig. 1, and time was allowed after each discharge for the gas to return to the initial temperature before the pressure was measured. Separate experiments on carbon dioxide carried out with and without the enclosed thermometer proved that the presence of the thermometer itself had no influence upon the establishment of the equilibrium pressures.

In the experiments recorded in Section E, Table III, a peculiar afterglow was observed which persisted for about four seconds at 0.5 mm. after the current had been cut off. The length of time varied somewhat with the pressure within the bulb. The afterglow had more of a yellowish tinge than was seen while the discharge was passing. Mixture F containing helium gave a pinkish glow, while carbon dioxide alone produced a bluish color.

To determine the effect of variation in the time of operation of the discharge, a series of experiments was conducted upon the decomposition of carbon dioxide, in which the discharge interval was varied from five seconds to ten minutes using the same initial pressure. Consideration of the following table of results shows clearly that at the end of two minutes equilibrium has been attained; the percentage decomposed, D, does not alter thereafter. Similar results were obtained when working at higher pressures.

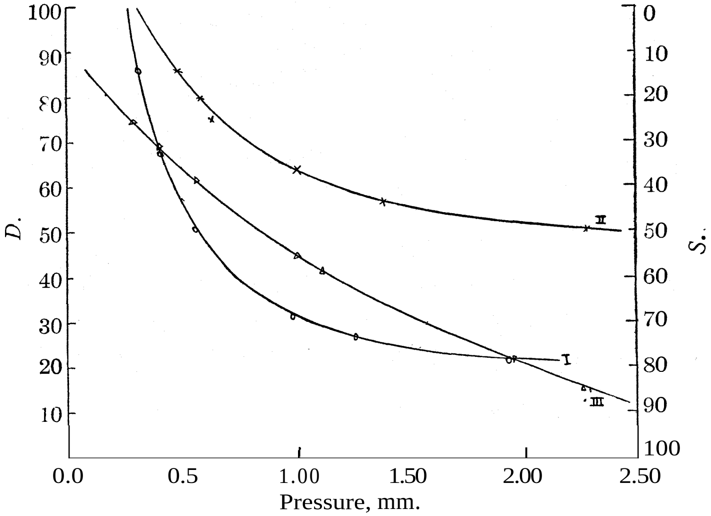

Fig. 3.—I, Synthesis: $CO/O_2 = 2$; II, synthesis: $CO/O_2 = 4$; III, synthesis: $CO/O_2 = 1$.

Finally, the effect upon the decomposition of change of wave length was observed by allowing the discharge to pass at 51 meters, the maximum afforded by the apparatus as constructed, instead of 34 meters, as in all the previous experiments. No appreciable alteration in the percentage decomposed was observed due to this change, as is indicated in Part B, Table IV.

Discussion of Results

The percentage of carbon dioxide decomposed, at a pressure *p*, plus the percentage synthesized from a mixture at a pressure, *p*, of two volumes

TABLE IV

A. EFFECT OF VARIATION IN TIME

Time	P_i	P_f	D
5 sec.	0.92	0.99	15.22
10 sec.	.92	1.035	24.9
15 sec.	.92	1.06	30.44
20 sec.	.92	1.07	32.61
30 sec.	.92	1.085	35.87
60 sec.	.92	1.09	37.0
2 min.	.92	1.10	39.13
5 min.	.92	1.10	39.13
10 min.	.92	1.10	39.13

B. EFFECT OF VARIATION IN WAVE LENGTH

P_i	P_f	$D, \lambda = 51$	$D, \lambda = 34$
0.82	1.00	43.90	43.90
1.02	1.205	36.27	36.40

of carbon monoxide plus one volume of oxygen are in all cases practically equal to 100%. Hence, we may assume that we are dealing with an equilibrium

$$2CO + O_2 \rightleftharpoons 2CO_2$$

The addition of carbon monoxide to the dissociating mixture decreases the amount of carbon dioxide decomposed and an excess of carbon monoxide in the synthesis of carbon dioxide increases the percentage of carbon dioxide synthesized.

Likewise, additional oxygen decreases the amount of decomposition of carbon dioxide but does not increase the amount of synthesis. Oxygen reduces the amount of decomposition relatively more than carbon monoxide. This is in contradiction to the mass action law, a fact which is in agreement with the observations of other workers in this field. If a complex, $[(CO_2)_x \cdot (O_2)_y]$, were formed by the union of CO_2^+ and O_2^-, we may assume that the energy used in its formation is wasted, as far as the dissociation of carbon dioxide is concerned. Similarly, the formation of $[(CO)_x \cdot (O_2)_y]$ by the union of CO^+ and O_2^- would decrease the extent of synthesis of carbon dioxide. This hypothesis is supported by the data at hand.

Helium increases the amount of decomposition of carbon dioxide and likewise decreases the amount of synthesis. Since helium has a high ionization potential, it may be assumed that it gives up any energy primarily absorbed to further disrupt carbon dioxide when it returns to its stable state.[5]

Nitrogen also caused an increase in the amount of carbon dioxide decomposed, but the process here is obscured by the probability of complicating reactions between the nitrogen and the other gases, especially

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[5] Cf. Brewer and Westhaver, *J. Phys. Chem.*, **34**,153 (1930).

oxygen. It is not surprising, therefore, that in this case the amount of decomposition and amount of synthesis do not equal 100%, as with helium. In view of these facts, we have omitted the data until the phenomena can be further investigated.

Summary

1. An apparatus suitable for producing a high frequency oscillatory electrodeless discharge has been described.

2. Under the influence of this discharge, the equilibrium

$$2CO + O_2 \rightleftharpoons 2CO_2$$

has been shown to be established, and data for this equilibrium at various pressures are given.

3. Variation in the length of time of discharge indicates that the reaction is brought to equilibrium in two minutes. Five minutes was adopted as the standard interval in these experiments.

4. The results obtained by variation in the percentage composition of the gas mixtures employed are not in agreement with the law of mass action. K_p is not a constant, but shows a decrease with increasing values of the equilibrium pressures.

5. Increased pressure decreases the extent of decomposition of carbon dioxide and increases the extent of synthesis, a fact, however, which is only in qualitative agreement with the law of mass action.

6. An inert gas, such as helium, displaces the equilibrium in the direction of increased decomposition of carbon dioxide.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OR THE UNIVERSITY OF ILLINOIS]

THE VAPOR PRESSURE OF SODIUM. LOW PRESSURE MEASUREMENTS WITH THE ABSOLUTE MANOMETER

BY WORTH H. RODEBUSH AND WM. F. HENRY

RECEIVED JUNE 2, 1930 PUBLISHED AUGUST 5, 1930

The reliable measurements on the vapor pressure of sodium at pressures below 0.1 mm. have all been made by the effusion method of Knudsen and the vapor pressures can only be calculated by assuming some value for the vapor density. Rodebush and Walters[1] have shown that the assumption of normal density for sodium at low pressures is justified, but it seemed desirable to check this by a direct measurement of the vapor pressure. This measurement presented an excellent opportunity to try out the absolute manometer described by Rodebush and Coons.[2]

For the measurement of vapor pressure the design of the gage was altered from that originally described, by inverting the arrangement of

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[1] Rodebush and Walters, THIS JOURNAL, 52,2654 (1930).

[2] Rodebush and Coons, *ibid.*, 49, 1953 (1927).

disk and seat. The disk was constructed of quartz instead of graphite. The arrangement of the apparatus is shown in Fig. 1. The substance whose vapor pressure was to be determined was placed in the flask F. The temperature of the furnace was regulated by hand and temperatures were measured with a chromel–alumel thermocouple which had been carefully calibrated at a series of fixed points. The furnace was well insulated so that its temperature changed slowly. Temperatures were read immediately before and after each measurement and the two readings usually differed by less than 0.5°. In order to prevent condensation of the saturated vapor on the movable disk or its suspension, a special heating coil was placed at J.

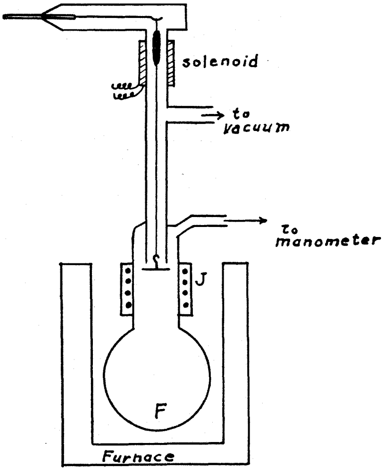

Fig. 1.

The mercury manometer shown in Fig. 1 was for the purpose of admitting air to the system at low pressure when the gage was calibrated against a McLeod gage. In addition the gage was calibrated by measuring the vapor pressure of mercury over the range 70–100°. The two calibrations were in excellent agreement.

The sodium was introduced into the apparatus by distillation with the customary precautions to avoid contamination. The results of the measurement are given in Table I and a plot of the data is shown in Fig. 2. The straight line in Fig. 2 is the graph of the equation

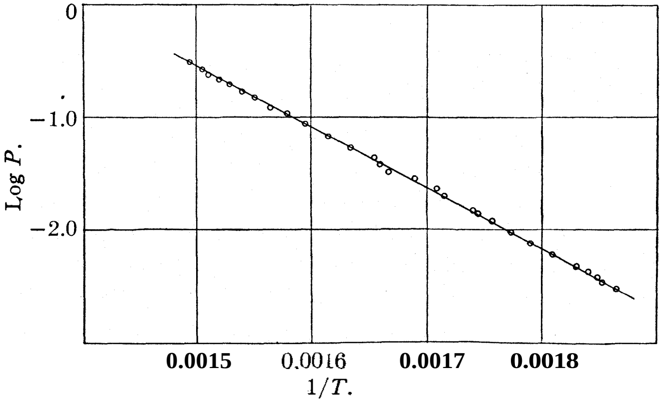

Fig. 2.

$$\log p_{\text{mm.}} = 7.551 - \frac{5400}{T}$$

TABLE I

VAPOR PRESSURE OF SODIUM

Temp., °C.	Pressure, mm.	Temp , °C.	Pressure, mm.	Temp., °C.	Pressure, mm
396.5	0.3025	346.0	0.0677	296.5	0.01205
392.0	.2700	339.0	.0538	291.0	.00955
389 5	.2400	331.0	.0438	286.0	.00760
384.0	.2195	329.5	.0381	280.0	.00603
381.0	.1952	323.0	.0332	273.0	.00480
376.0	.1702	319.5	.0289	271.0	.00427
371.0	.1517	312.5	.0235	268.0	,00381
366.0	.1233	310.0	.02045	267.0	.00347
360.0	.1074	302.0	.01520	263.0	.00303
354.0	.0876	300.0	.01385		

given by Rodebush and Walters as the best representation of all previous data. It is evident from Fig. 2 that the new data confirm the correctness of the equation in a most satisfactory manner.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

ISOTOPES AND THE PROBLEM OF GEOLOGIC TIME

BY CHARLES SNOWDEN PIGGOT

RECEIVED JUNE 4, 1930 PUBLISHED AUGUST 5, 1930

Time can be estimated only by reference to some change, and geologic time is no exception. Any change demands a beginning and an ending condition, and a rate.

The phenomena which fulfil these conditions throughout the great lengths of geologic time are: (1) denudation and sedimentation, (2) the salting of the ocean and *(3)* radioactive disintegration of uranium into lead.

They are all of the hour-glass principle and if we could measure the amounts involved at the beginning and at the end—and ascertain the rate of change—the problem of geologic time would be a very simple one. But of the three, only the last can be measured with the accuracy necessary to inspire confidence in the result. We can well imagine what a difficult task it was to arrive at any accurate estimate of the amount of material that had been eroded from the highlands and deposited in the hollows to form sedimentary formations, particularly when it was known that these sedimentary formations often became, in turn, highlands from which further erosion took place.

It was not much easier to estimate the rate at which sodium was being leached from the igneous rocks and carried into the sea. It was easy to determine the sodium in a rock, and in a sample of sea water; but to decide on the amount of rock and the amount of sea was not so simple, nor did such minor corrections as the great salt deposits necessitated make the problem any easier for the old-time geologist.

With the discovery of radium and the unraveling of the mysteries of radioactive disintegration, and especially the demonstration of the relationship existing between uranium and lead, the geologist felt that at last he had an accurate timepiece, of relative simplicity, and one capable of most refined measurements.

And so he had, compared with the ones he had been struggling with before, and the new tool was adopted with enthusiasm. However, as refinement of measurement and accuracy increased, factors which at first had been ignored began to assume increasing importance, and it is some of these minutiae that I wish to discuss now.

If it were only a case of ascertaining the amount of uranium and the amount of lead present in a mineral and applying that information to the known rate of change of the uranium–radium–lead series the problem would resolve itself into simply one of refined chemical analysis; but some thorium is almost always present in uranium minerals, which, besides complicating the chemical analysis, makes necessary a correction to take care of that portion of the total lead that came from the thorium. This correction factor (0.38 Th) is shown in the formulas given below.

SIMPLIFIED FORMULAS (APPROXIMATE) FOR CALCULATION OF GEOLOGIC TIME

$$\text{Age} = \frac{\text{Pb}}{\text{U} + 0.38\ \text{Th}} \times 7400 \text{ million years} \tag{1}$$

$$\text{Age} = \frac{\log(\text{U} + 0.38\ \text{Th} + 1.55\ \text{Pb}) - \log(\text{U} + 0.38\ \text{Th})}{6.5} \times 10^{11} \text{ years} \tag{2}$$

It is supposed to represent the amount of uranium which is equivalent in lead-producing capacity to 1 g. of thorium. Unfortunately, this value is not universally accepted, nor is the time required for a given amount of thorium to form its corresponding amount of lead known with satisfactory accuracy. Therefore the inevitable presence of thorium introduces an annoying element of uncertainty into any formula that may be devised. So, if we could eliminate consideration of the thorium altogether, it would be a great relief.

Furthermore, there is no actual measure of that proportion of the total lead which is known to have been produced by the uranium alone. If this latter could be determined by actual experimental measurement, the thorium could be disregarded altogether and the only other uncertainty which would remain inherent and unmeasured in this method would be the existence of possible isotopes of uranium which have disintegrated at a different rate in the past from the uranium which we know today.

We attempted to accomplish all this by the identification and the determination of the isotopes of lead. As this had not been done, we first began work on "ordinary" lead. The problem was to get the lead into some volatile form with the proper polarity to enable it to be swept along in the stream of positive rays in a mass spectrograph.

Lead tetramethyl was made and the technique developed to a point where a workable quantity could be obtained from 5 g. (or less) of lead chloride.[1]

Dr. F. W. Aston,[2] F.R.S., kindly consented to cooperate and in July, 1927, he carried out several experiments with this material. These demonstrated very clearly the existence of the three anticipated isotopes of masses 206, 207 and 208 in the approximate ratios of 4, 3 and 7, respectively, as shown in Table I.

TABLE I

RELATIVE PROPORTIONS OF LEAD ISOTOPES

	Percentage of isotopes Pb 206	 Pb 207	 Pb 208
Ordinary lead	28.6	21.4	50.0
Radioactive lead	86.8	9.3	3.9

The existence of isotope 207 demonstrated that the atomic weight of 207.2 was not a statistical mean of isotopes 206 and 208 only.

The next step was to do the same for "radioactive" lead. This was obtained from a very pure sample of Norwegian broggerite, a mineral which is high in uranium but contains very little thorium. In Professor Aston's mass spectrograph this lead also revealed isotopes 206, 207 and 208. The presence of isotope 207 in this radioactive lead was somewhat of a surprise, but when it was noticed that the relative proportions were radically different, its presence took on added significance.[3]

These results demonstrate that isotope 207 exists even in lead of radioactive origin. Consequently it must have a corresponding source, and this source is now assumed to be an isotope of uranium which is the parent substance of the actinium series.

To quote from Aston's report in Nature of March 2, 1929: "The line 207 is of peculiar significance. It cannot be due to the presence of lead as an impurity, for in ordinary lead 208 is about twice as strong as 207, neither can it be the product of radium or thorium. It is difficult to resist the natural conclusion that it is the end-product of the only other known disintegration, namely, that of actinium. If this is so it settles the mass numbers of the members of this series, that of protoactinium being 231."

We can now assume that the actino-uranium (parent substance of the actinium series) has a mass of 239 and is converted into a mass 235 in consequence of an alpha change followed by two beta changes, as is the

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[1] This was done for me by Mr. S. C. Witherspoon, then of the U. S. Chemical **Warfare** Service.

[2] Aston, ***Nature,*** 120, 224 (1927).

[3] Aston, *ibid.*, 123, 313 (1929).

case in the uranium–radium series, or a mass 235 to begin with, which passes through an alpha and a beta transformation to form protoactinium.

Both alternatives are suggested and discussed by Rutherford.[3]

By whatever method they were formed, we now are certain of three leads each legitimately descended from its corresponding parent substance, as is illustrated diagrammatically in Table II.

TABLE II

ORIGINS OF THE THREE LEAD ISOTOPES

$$\begin{tikzcd} U_{238} \arrow[d, "8\alpha"'] & U_{239 \text{ or } 235} \arrow[d, "8\alpha \text{ or } 7\alpha"'] & Th_{232} \arrow[d, "6\alpha"'] \\ Pb_{206} & Pb_{207} & Pb_{208} \end{tikzcd}$$

By means of the mass spectrograph and an intensimeter we are now able to determine the amount of Pb_{206} in the lead separated by analysis of a uranium mineral, but as yet we cannot determine the actual U_{238} from which it came. This will require the determination of the isotopes of uranium—as yet not accomplished.

Dr. Moses Gomberg is very generously coöperating with us in an effort to secure some volatile organic compound of uranium which could serve as the tetramethyl did for the lead, but uranium is infinitely more difficult to cope with than lead, because of its multiplicity of valences and its annoying habit of combining with itself.

The field of the organic compounds of uranium is practically untouched.

Should the determination of the isotopes of uranium be accomplished, we would then have a measure of the particular uranium from which the Pb_{206} came, and our formula would be simplified thereby. Further knowledge of the isotopes of uranium would be of great value in many lines of research, but to mention only one having tremendous significance for the problem of geologic time, it is very important to learn whether or not the U_{238}–Pb_{206} series disintegrates at a different rate from that determined for the mixture of isotopes as a whole.

WASHINGTON, D. C.

NOTES

Historical Note on the Equilibrium between Methanol and its Decomposition Products.—In a recent paper[1] Messrs. B. S. Lacy, R. G. Dunning and H. H. Storch state that my determinations of the equilibrium constants of the reactions

$$2H_2 + CH_3OOCH \longrightarrow 2CH_3OH \qquad (1)$$

and

$$CO + CH_3OH \longleftarrow CH_3OOCH \qquad (2)$$

were carried out later than 1922.

May I be allowed to state that the work contained in my paper[2] published in 1926 on Reaction 1 was carried out during the spring of 1917 by myself, and the work on Reaction 2 during the spring of 1918 by Mr. Arne Olsen and myself.

I may perhaps add that my equations are expressions of the concentration constants and thus may be easily transformed into equations for the pressure constants without recalculation of the single experimental values and finally that Lacy and co-workers have included in their Fig. 1 my experiments Nos. 16 and 17, which as stated in my paper, ought not to be included on account of obvious loss in activity of the catalyst.

CHEMICAL LABORATORY OF THE UNIVERSITY J. A. CHRISTIANSEN
COPENHAGEN, DENMARK

RECEIVED APRIL 23, 1930
PUBLISHED AUGUST 5, 1930

A Note on the Preparation of Silver-Free **Copper.**—The preparation of standard solutions for the estimation of small amounts of silver in copper spectrographically requires silver-free copper. A number of commercial samples of copper were tested and all contained silver. Even one obtained from England which the vendors stated was apparently silver-free gave a spectrogram which showed distinct silver lines. It was therefore deemed advisable to experiment on the separation of the last spectrographic traces of silver from copper. The following procedure successfully accomplished this result.

Commercial copper sulfate was recrystallized three times and a spectrogram made from it showed only a small amount of silver (about 0.004% was found later). Four hundred grams of this recrystallized sulfate was made up to two liters with 5% nitric acid, the solution divided into eleven portions and electrolyzed for one hour between platinum electrodes with a current of 0.05 ampere at seven volts. The electrodes were removed from the solution, washed, and the small deposit was dissolved in nitric acid. The clean electrodes were put back into the solutions and the electrolysis con-

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Lacy, Dunning and Storch, THIS JOURNAL, 52,926 (1930).

[2] Christiansen, J. Chem. *Soc.*, 413 (1926).

tinued for sixteen hours, after which the deposits were dissolved as before. In this manner seven fractions were made. Each of these fractions was evaporated to dryness and ignited to convert the copper nitrate to oxide. The weight of copper oxide obtained in each of the fractions together with the current strength and the duration of electrolysis is shown in the table. The estimated silver content of the copper in each fraction is shown in the last column. The residue was obtained by evaporating the whole two liters of solution from which the copper had been deposited to dryness and igniting.

TABLE I

EXPERIMENTAL DATA

No.	CuO, g.	Time, hours	Current, amp.	Silver, %
1	1.5	1	0.05	0.125
2	8	16	.05	.008
3	4	8	.05	.0005
4	9	17	.05	.0002
5	12	23	.05	none
6	66	24	.2	none
7	24	9	.2	none
Residue	1.5	..	..	.015

Copper oxide from fraction six was reduced in a silica tube by means of hydrogen, the copper was melted in a silica crucible in an induction furnace and drawn into a bar from which electrodes were cut. An arc spectrogram of these copper electrodes showed no trace of the silver line at 3281. Copper itself gives a faint line which might be confused with the silver line at 3383. The most persistent silver line is at 3281. The presence of as little as 0.0002% silver in copper can be detected by means of this line when the solution method of comparison is employed.

The silver was estimated by comparing the intensity of this line in a spectrogram given by a measured amount of the unknown with its intensity in spectrograms of measured amounts of solutions of known silver content. The amount used in each case was one-tenth of a cubic centimeter of solution containing 10% of copper. This was placed in a hollowed graphite electrode, dried in an oven at 110° and then arced for three minutes using a current of ten amperes at 50 volts. This is the well-known method described by C. C. Nitchie ["Quantitative Analysis with the Spectrograph," *Ind. Eng. Chem.*, **Anal.** Ed., 1, 1 (1929)].

CONTRIBUTION FROM THE
MICHIGAN COLLEGE OF MINING AND TECHNOLOGY
HOUGHTON, MICHIGAN

BART PARK

RECEIVED MAY 19, 1930
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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

OXIDATION OF UNSATURATED COMPOUNDS. II. PREPARATION AND CONFIGURATION OF THE 3-HALOGENO DERIVATIVES OF CROTONIC ACID

BY GÉZA BRAUN[1]

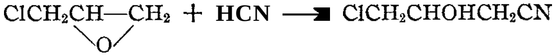
RECEIVED NOVEMBER 27, 1929 PUBLISHED AUGUST 5, 1930

In the first publication of this series[2] the oxidation of crotonic and isocrotonic acids with chlorates and perbenzoic acid was reported. There is no known method for the establishment of the configurations of the *dl*-1,2-dihydroxybutyric acids which resulted. However, the results which were obtained were so harmonious that it was possible to assign configurations to these acids with a considerable degree of assurance. For the purpose of the exact chemical proof of configuration it would be necessary to convert these compounds into the tartaric acids in such a way that no change of configuration could take place during these operations. Unfortunately these changes could not be accomplished by direct oxidation of the dihydroxybutyric acids with dilute nitric acid because the methyl group is completely eliminated in the oxidation. It seemed therefore to be necessary to synthesize compounds having a substituent in the methyl group—these would be the derivatives of threonic and erythronic acids—the configurations of which could be shown by oxidation to the tartaric acids. Their relationship to the dihydroxybutyric acids on the other hand could be demonstrated by reduction. For this indirect proof of configuration only the 3-halogeno derivatives of threonic and erythronic acids could come into consideration, making a connection between the tartaric and 1,2-dihydroxybutyric acids.

These halogeno-tetronic acids are as yet unknown. For their synthesis the oxidation of the corresponding 3-halogeno-crotonic acids seemed to offer the most practicable method, and it became necessary therefore to study the preparation and properties of these unsaturated acids.

I. Preparation of 3-Chlorocrotonic Acid

This acid was first prepared by Lespieau[3] by means of the operations indicated



$$ClCH_2\underset{\diagdown O \diagup}{CH{-}CH_2} + HCN \longrightarrow ClCH_2CHOHCH_2CN \qquad (1)$$

$$ClCH_2CHOHCH_2CN \xrightarrow[\text{in alc.}]{HCl} ClCH_2CHOHCH_2COOC_2H_5 \qquad (2)$$

$$ClCH_2CHOHCH_2COOC_2H_5 \xrightarrow{P_2O_5} ClCH_2CH{=}CHCOOC_2H_5 \qquad (3)$$

$$ClCH_2CH{=}CHCOOC_2H_5 \xrightarrow{KOH} ClCH_2CH{=}CHCOOH \qquad (4)$$

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[1] International Research Fellow in Organic Chemistry from Hungary, 1926–1928.

[2] Géza Braun, THIS JOURNAL, 51, 228 (1929).

[3] Lespieau, *Bull. soc. chim.*, [3] 33, 466 (1905).

These reactions are described by Lespieau only in a general way. The yields must have been rather low but, because all the operations involved are of general interest in the field of preparative organic chemistry, it was decided to study and, if necessary, modify the original procedure to improve the yield. A new process is reported which makes it possible to obtain the 3-chlorocrotonic acid from the 2-hydroxy-3-chloro-n-butyronitrile in 32% yield.

(1) **2-Hydroxy-3-chloro-*n*-butyronitrile.**—Lespieau's[3,4] original method has the great disadvantage that the handling of anhydrous hydrogen cyanide above its boiling point is very inconvenient. The new procedure avoids this; it involves the treatment of dichlorohydrin with sodium cyanide in aqueous suspension. The desired product is separated from the dinitrile, which is formed to some extent, by fractionation and is obtained in 25% yield.

(2) Ethyl **2-Hydroxy-3-chlorobutyrate.—The** ester was prepared by treatment of the nitrile with dry hydrogen chloride in absolute alcohol according to Stieglitz and Carr[5] but without the isolation of the pure imino-ester hydrochloride. The yield of pure ester was as high as 80–85% of the theoretical.

(3) Ethyl **3-Chlorocrotonate.**—In the preparation of this ester the best results were obtained when only 70% of the theoretical amount of phosphorus pentoxide was used for the dehydration of ethyl 2-hydroxy-3-chlorobutyrate. The purified reaction product was obtained in good yield (62.5%), but it proved to be a mixture of unsaturated halogeno esters; saponification yielded two isomeric halogeno acids. There are two possibilities in the dehydration of ethyl 2-hydroxy-3-chlorobutyrate: the reaction may involve carbon atoms 2 and 1 or carbon atoms 2 and 3, yielding ethyl 3-chlorocrotonate, $CH_2ClCH{=}CHCOOC_2H_5$, or ethyl 3-chloro-vinylacetate, $ClHC{=}CHCH_2COOC_2H_5$, respectively. There is also a possibility of the formation of ethyl 3-chloro-isocrotonate but the formation of this under the conditions is very improbable. It was estimated on the basis of the saponification results that the ester mixture contained about 80% of ethyl 3-chlorocrotonate.

(4) Saponification of the Unsaturated Esters.—This is the most delicate step in the synthesis. The esters are very resistant toward hydrolysis by acids. The saponification proceeds rapidly in alkaline solution but extreme care must be taken to protect the organic halogen. It was found that barium hydroxide below 0° gives excellent results. The 3-chlorocrotonic acid (m. p. 83°) is obtained in high yield and it is possible to isolate from the mother liquor an isomeric unsaturated halogeno acid of m. p. 10° (very probably the 3-chloro-vinylacetic acid). A study of this acid is in progress.

[4] See also Hormann, Ber., **12,** 23 (1879).

[5] Carr, Doctor's Dissertation, University of Chicago, 1910.

The barium hydroxide method may also be used in the saponification of ethyl 3-bromo- and ethyl 3-iodocrotonates; the yields of the pure acids are over 50% of the theoretical.

II. The Preparation of 3-Bromo- and 3-Iodocrotonic Acids

(1) **The** 3-Bromocrotonic acid was prepared in essentially the same manner as the 3-chlorocrotonic acid. The preparation of the dibromohydrin, which is the starting material in the preparation of 3-bromocrotonic acid, has been greatly improved. It is possible to obtain it now from glycerin in 54% yield, while the original method of Aschan[6] gave only 12% and Lespieau's method[7] about 21%. The purity of the product obtained was controlled by its conversion into epibromohydrin according to Fourneau and Tiffeneau.[8]

(2) 3-Iodocrotonic Acid.—The preparation of this acid is based on the fact that the 3-chlorocrotonic acid precipitates sodium chloride from an acetone solution of sodium iodide and the chloro acid is converted into 3-iodocrotonic acid by this process. The same reaction may be carried out with the 3-bromocrotonic acid, when the sodium bromide precipitates instantaneously. The yields of 3-iodocrotonic acid are in both cases almost quantitative.

The ethyl 3-iodocrotonate is obtained from ethyl 3-chlorocrotonate by the procedure described above in good yield.

Thus three 3-monohalogeno derivatives of crotonic acid are known. The bromo has the lowest (74°), the iodo the highest 108.5°), and the chloro an intermediate (83°) melting point.

III. Configuration of 3-Halogeno-crotonic Acids

The 3-chlorocrotonic acid may be reduced with palladium-activated hydrogen in alkaline solution to crotonic acid according to Rosenmund and Zetzsche. This shows clearly that the 3-chlorocrotonic acid belongs to the crotonic acid series and has the *trans* configuration according to Auwers and Wissebach.[9] It is a remarkable fact that the reduction of 3-bromocrotonic acid proceeds much more slowly and the 3-iodocrotonic acid not at all under the conditions in which the 3-chlorocrotonic acid is easily reducible. This will be the subject of a future study.

The relationship between these halogeno-crotonic acids is shown by converting the 3-chloro- and 3-bromocrotonic acids into the 3-iodocrotonic acid in an acetone solution of sodium iodide, proving that all these acids have the *trans* configuration.

The preparation of 3-chlorocrotonic acid was attempted by the partial

[6] Aschan, ***Ber.*, 23,** 1826 (1890).

[7] Lespieau, *Ann. chim.*, [7] 11, 236 (1897).

[8] Fourneau and Tiffeneau, *Compt.* rend., 140, 1595 (1905).

[9] Auwers and Wissebach, *Ber.*, 56, 715 (1923).

reduction of Auwers' 3,3-dichlorocrotonic acid.[10] Unfortunately no definite compound could be isolated directly from the reduction product. However, when the crude product was treated with sodium iodide in acetone solution, the pure 3-iodocrotonic acid was isolated, which could have been derived only from the 3-chlorocrotonic acid. This established the fact that the 3-chlorocrotonic acid is an intermediate product in the reduction of 3,3-dichlorocrotonic acid to crotonic acid.

In the preparation of the 3,3-dichlorocrotonic acid the yields were invariably as high as 80–85%, whereas Auwers reports only 50–60%. The improvement is probably due to the fact that zinc was added during the reduction very slowly under violent stirring, so the possibility of local overheating was reduced to a minimum.

Experimental Part

I. Preparation of 3-Chlorocrotonic Acid

(1) **2-Hydroxy-3-chlorobutyronitrile.**—(a) A mixture of 500 g. of epichlorohydrin and 145 g. of anhydrous hydrogen cyanide was heated in a dilute sodium hydroxide bath to 75–85° in a thick-walled pyrex tube for ninety hours. The yield after two fractional distillations was 420 g. of nitrile, b. p. 138–142° at 14 mm., or 65%.

(b) From Dichlorohydrin.—Three hundred grams of dichlorohydrin was suspended in 500 cc. of water and, under violent stirring, 100 g. of sodium cyanide was added in the course of about twenty minutes at 60°. The temperature was then gradually raised to 100° in about two hours. The water and unchanged dichlorohydrin were now removed at reduced pressure and the residue dissolved in alcohol–ether mixture. The filtrate from the sodium chloride was concentrated at reduced pressure, the residue dissolved in ether and the ethereal solution fractionated; the yield was 60 g. of nitrile, b. p. 138–142° at 14 mm., or 25% of the theoretical on the basis of sodium cyanide. This product may be used in the preparation of 3-chlorocrotonic acid. For analysis it was redistilled at 2 mm. pressure (b. p. 110–112°).

Anal. Subs., 0.5050, 0.5863: AgCl, 0.5888, 0.6854. Calcd. for C_4H_6ONCl: Cl, 29.67. Found: Cl, 28.84, 28.92.

The residue from the above nitrile was distilled further at 2 mm. pressure; 30 g. of a viscous, yellow sirup, b. p. 160–180°, was obtained. This was not investigated at the time.

(2) **Ethyl 2-Hydroxy-3-chlorobutyrate.**—Five hundred grams of 2-hydroxy-3-chlorobutyronitrile (from epichlorohydrin) was dissolved in 260 cc. of absolute alcohol and 500 cc. of dry ether, the mixture cooled to −15° and slowly saturated with dry hydrogen chloride (in about six to eight hours). Then the ether and excess hydrochloric acid were removed under reduced pressure at room temperature as far as possible (in about five hours) and the residue—a very thick sirup—was dissolved in one liter of water and the solution kept at 45–50° for about half an hour. Then the oil was separated and united with the ethereal extract of the aqueous solution. The ethereal solution was now washed with sodium bicarbonate, dried with sodium sulfate and fractionated; yield, 564 g. of colorless ester, b. p. 120° at 15–16 mm. or 81%. In 100-g. lots the yield of ester was as high as 85%. The crude nitrile from dichlorohydrin gives the ester in about 70–75% yield.

(3) **Ethyl 3-Chlorocrotonate.**—To 200 g. of crude ethyl-2-hydroxy-3-chlorobutyrate in a 1-liter round-bottomed flask, 100 g. of phosphorus pentoxide was added in 10–20

g. lots under violent shaking. The temperature rose to about 100°. Then the flask was put in a 190° oil-bath and after ten minutes' heating the product was drawn over by vacuum as fast as the foaming of the mass permitted. The distillation was continued at reduced pressure until no more material came over. The yield of a pale yellow distillate was 125–128 g. The united distillates of two experiments gave after two fractional distillations 223 g. of unsaturated ester, b. p. 80° at 10 mm. (62.5%) and 23 g. of a fraction above 100° at 10 mm.

The unsaturated ester was redistilled at 2 mm. pressure. It distilled at 66–68° to a small residue.

Anal. Subs., 0.5161, 0.6799: (after reduction with sodium in absolute alcohol) 37.82, 45.43 cc. of 0.1 N $AgNO_3$. Calcd. for $C_6H_9O_2Cl$: Cl, 23.88. Found: Cl, 23.73, 23.70.

The high-boiling fraction partially crystallized during the distillation. The mixture was cooled in ice and after five hours' standing the crystals were separated by filtration, pressed between filter paper and recrystallized from 30 cc. of ligroin (60–110°); 7 g. of crystals, m. p. 83.5°, was obtained (2.5%); mixed m. p. with 3-chlorocrotonic acid (m. p. 83°), 83°.

Anal. Subs., 0.3294, 0.4514: 27.15, 37.3 cc. of 0.1 N $AgNO_3$. Calcd. for $C_4H_5O_2Cl$: Cl, 29.42. Found: Cl, 29.23, 29.30.

One g. of the crystals was dissolved in 7 cc. of acetone which contained 2.5 g. of sodium iodide, etc. (see below); 1.1 g. of yellow crystals, m. p. 108–108.5°, was obtained; mixed m. p. with the pure 3-iodocrotonic acid (m. p. 108°), 108°.

(4) Saponification of Ethyl 3-Chlorocrotonate. (A) With Potassium Hydroxide.—Two hundred and fifty grams of ester was dissolved in 200 cc. of absolute alcohol, the solution cooled to −15° and, under violent stirring, 100 g. of potassium hydroxide in 300 cc. of water was added in about one and one-half hours. After one and one-half hours' stirring at −15°, the stirring was continued at 0° for two hours, when all of the potassium hydroxide was used up. The mixture was diluted with 200 cc. of water and extracted three times with ether. The ethereal solution gave 50 g. of unchanged ester, b. p. 90° at 15 mm.

The aqueous solution was acidified with ice cold dilute sulfuric acid (calcd. amount) and the solution extracted with ether. (After extraction of the unsaturated acids the aqueous solution contained according to titration potassium chloride corresponding to about 15% of ester used.) The ethereal extract was dried with sodium sulfate, etc. The residue was dissolved in hot ligroin (60–110°) in the presence of sodium sulfate, the solution decanted and the operation repeated several times. The ligroin solution deposited yellowish crystals at −15° which were recrystallized from ligroin (for 50 g. of pure material about 800 cc. of boiling range 60–110° or 2 liters of 40–50°). The yield was 66 g. of white crystals, m. p. 83°, or 40%.

Titration. Subs., 0.2505, 0.2998: 20.32, 24.24 cc. of 0.1 N alkali. Calcd. mol. wt. for $C_4H_5O_2Cl$: 120.5. Found: 123.5, 123.6.

Anal. Subs., 0.4431, 0.3123: 36.3, 25.5 cc. of 0.1 N $AgNO_3$. Subs., 0.1252, 0.1499 (titrated with bromine water, see ref. 2): 20.62, 24.61 cc. of 0.1 N $Na_2S_2O_3$. Calcd. for $C_4H_5O_2Cl$: Cl, 29.42; iodine number, 210.6. Found: Cl, 29.06, 28.96; iodine number, 209, 208.4.

The united ligroin mother liquors of the 83° crystals gave about 40 g. of a liquid product (dried at two mm. for five hours). This acid deposited large amounts of crystals at −20°; the crystallized product showed the same analytical data as the 3-chlorocrotonic acid (see later in connection with the barium hydroxide saponification).

(B) With Barium Hydroxide at Room Temperature.—The procedure is the same as is described under (C) except that the temperature was 0° at the beginning and about 20" at the end of the reaction. Thirty g. of ester treated with 32 g. of barium hydroxide gave 8.5 g. of crystalline product, m. p. 82° (43% of theoretical) with 14 g. of white powder insoluble in ether and water. Six grams of unchanged ester was recovered.

(C) With Barium Hydroxide Below 0°.—One hundred grams of pure ester was emulsified by violent stirring in 700 cc. of 25% alcohol. In an apparatus fitted with mercury-sealed stirrer, and after the mixture had been cooled to −10°, 110 g. of finely powdered barium hydroxide was added in the course of about an hour.. Then the mixture was stirred for ten hours at −2° and afterwards for six to ten hours at 1–2°, *i. e.*, until all of the barium hydroxide was consumed. The procedure from this point is exactly the same as described under (A). The yield was 44 g. of 3-chlorocrotonic acid, m. p. 78–80° (60%), and 18 g. of liquid acid, m. p. 2–5° (25%). Ten g. of unchanged ester was recovered. The acid 78–80° gave 40 g. of product, m. p. 83°, from low-boiling ligroin.

The liquid acid was dissolved in 25 cc. of low-boiling ligroin, the mixture cooled to −15° and the crystals separated as quickly as possible. By repetition of this crystallization 10 g. of product of m. p. 10° was obtained. The melting point could not be changed any further.

Anal. Subs., 0.3039: 24.35 cc. of 0.1 *N* alkali. Calcd. for $C_4H_5O_2Cl$, mol. wt., 120.5. Found: mol. wt., 124.8. Subs., 0.3734: 30.23 cc. of 0.1 N silver nitrate. Subs., 0.3092: 51.0 cc. of 0.1 *N* $Na_2S_2O_3$. Calcd. for $C_4H_5O_2Cl$: Cl, 29.42; iodine number, 210.6. Found: Cl, 28.7; iodine number, 209.3.

Preparation of **3,3-Dichlorocrotonic** Acid.—Sixty grams of 3,3,3-trichlorocrotonic acid (m. p. 114°) was dissolved in 120 cc. of alcohol and then 30 cc. of water and 46 cc. of glacial acetic acid were added. In the course of about twenty minutes 27 g. of zinc dust was added in very small portions at 56° while the solution was violently stirred. After addition of zinc the solution was stirred for fifteen minutes, then cooled, extracted with ether (after addition of 600 cc. of water), and the ethereal solution washed three times with small amounts of water, etc. The residue of the ethereal solution gave 40 g. of white crystalline product at 110° under 2 mm. pressure. In other similar experiments 42-43 g. of this product was obtained, corresponding to an average yield of 85% of the theoretical. Recrystallization from low-boiling ligroin at −15° yielded 37.5–40 g. of crystals, m. p. 4243°. The recrystallized acid is very stable and may be stored for years, whereas the crude product begins to decompose in several months.

II. Preparation of 3-Bromocrotonic Acid

(1) Preparation of **Dibromohydrin.**—To a mixture of 1600 g. of glycerin and 150 g. of red phosphorus, 750 cc. of bromine is added in about seven to eight hours under effective stirring and moderate cooling, so that the reaction mixture is always hot. Then the mixture is heated on the water-bath until all of the bromine disappears (three hours). After this the solution is cooled to 40–50°, 150 cc. of bromine is added in one operation and the mixture is allowed to stand at room temperature overnight. After the solution is heated for three hours on the water-bath, the reaction mixture is distilled under reduced pressure until the oil-bath reaches 180° and the residue shows the first sign of decomposition. The distillate is now neutralized with sodium bicarbonate, the aqueous solution separated from the oil and extracted with a small amount of ether. This ethereal extract is united with the oil, dried with sodium sulfate and purified by fractional distillation; yield, 2050 g. of colorless product, b. p. 110–112° at 20 mm., or 54%.

Epibromohydrin.—Four hundred and forty grams of dibromohydrin was dissolved in 1.2 liters of dry ether and, under violent stirring, 95 g. of finely powdered sodium hydroxide was gradually added in about fifteen minutes under ice cooling. The mixture was then stirred for one hour at room temperature. The sodium bromide was separated by filtration and the filtrate fractionated; yield, 204 g. of colorless mobile oil, b. p. 134–136°, or 75%

(2) **2-Hydroxy-3-bromo-*n*-butyronitrile.**—One thousand and eighty grams of dibromohydrin was suspended in 2 5 liters of water which contained 350 g. of potassium cyanide, etc , as is described in the case of the chloronitrile under (b). The solution became dark brown. The yield of redistilled product, b. p. 154" at 14 mm., was 93 g. or 16.5%. This was redistilled under 2 mm. pressure; 80 g. of colorless distillate, b. p. 117–118°, was obtained.

Anal. Subs., 0.4938, 0.4248: AgBr, 0.5643, 0.4843. Calcd. for C_4H_6ONBr: Br, 48.72. Found: Br, 48.64, 49.00.

(3) Ethyl **2-Hydroxy-3-bromobutyrate.**—Four hundred and thirty grams of crude 2-hydroxy-3-bromo-butyronitrile, b. p. 148–154° at 14 mm., was dissolved in 165 cc. of absolute alcohol and 250 cc. of ether and saturated with dry hydrogen chloride in exactly the same manner as in the case of ethyl 2-hydroxy-3-chlorobutyrate. The yield was 425 g. of yellow crude ester (dried at 100° for two hours at reduced pressure) or 77%. The crude ester boils at 94–96" at 2 mm. uith slight decomposition. The yield of colorless distillate after two fractionations was 70% of the crude ester.

Anal. Subs., 1.0917: AgBr, 1.0750. Calcd. for $C_6H_{11}O_3Br$: Br, 37.88. Pound: Br, 41.90.

(4) Ethyl **3-Bromocrotonate.**—To 75 g. of crude ethyl 2-hydroxy-3-bromobutyrate 25 g. of phosphorus pentoxide was added, under violent shaking, in two lots. The further procedure was the same as in the case of ethyl 3-chlorocrotonate. The united crude distillates of five experiments gave 98 g. of twice distilled pure ester, b. p. 80–82° under 2 mm., or 28.5%.

Anal. Subs., 0 4403, 0.4329: 22.03, 21.70 cc. of 0.1 N silver nitrate (after reduction with sodium in absolute alcohol). Calcd. for $C_6H_9O_2Br$: Br, 41.4. Found: Br, 40.00, 40.06.

The ester is soluble in all of the usual organic solvents except ligroin. It has a pleasant odor but causes blisters on the skin.

The residue from the distillation of the unsaturated ester deposited a small amount of crystals (probably 3-bromocrotonic acid).

(5) Saponification of Ethyl **3-Bromocrotonate.**—Twenty grams of ester was dissolved in 250 cc. of 25% alcohol and treated with 16 g. of powdered barium hydroxide below 0° in the same manner that is described in the case of ethyl 3-chlorocrotonate under (c). Six and a half grams of white crystals, m. p. 70–71°, was obtained from 200 cc. of ligroin (60–110°). This corresponds tu 44% of the theoretical.

The mother liquor of the crystals gave about 1 g. of liquid acid which partially crystallized in a freezing mixture; the total yield of unsaturated acids was 7.5 g. or 50% of the theoretical. Three grams of ester was recovered.

The crystals, m. p. 70°, were recrystallized from 70 cc. of hot ligroin. Five and nine-tenths grams of crystals (m. p. 74") was obtained.

Anal. Subs., 0.2335, 0.1364: 14.0, 8.2 cc. of 0.1 *N* alkali. Calcd. for $C_4H_5O_2Br$: mol. wt., 164.94. Found: mol. wt., 165.8, 165.3. Subs., 0.3737, 0.6293: 22.6, 38.00 cc. of 0.1 N of silver nitrate. Calcd. for $C_4H_5O_2Br$: Br, 48.45. Found: Br, 48.32, 48.25.

The 3-bromocrotonic acid (m. p. 74") crystallizes in large plates from ligroin. The crystals are very soluble in ether, chloroform, acetone, etc., but sparingly soluble in cold ligroin. The saturated aqueous solution contains at room temperature about 3% of the acid.

III. Preparation of 3-Iodocrotonic Acid

(1) Ethyl 3-Iodocrotonate.—Thirty grams of ethyl 3-chlorocrotonate was dissolved in 100 cc. of acetone which contained 32 g. of sodium iodide. The precipitation of sodium chloride started immediately and was finished in about an hour. The precipitate was now separated by filtration and washed with acetone; 9.5 g. of sodium chloride (80% of the theoretical) was obtained. The filtrate from the sodium chloride was poured into 500 cc. of ether; the ethereal solution was washed with sodium thiosulfate solution and then with water and finally dried with sodium sulfate. The residue from this solution, a dark orange ester, weighed 42 g. This crude product was fractionated under 2 mm. pressure; 12 g. of distillate was obtained from 85 to 90°, the rest boiled at 90–92° with slight decomposition. The distillate was much darker than the crude product.

Anal. of the crude product. Subs., 0.7263, 0.7836: 32.0, 34.1 cc. of 0.1 N silver nitrate. Calcd. for $C_6H_9O_2I$: I, 52.88. Found: I, 55.92, 55.5.

Anal. of fraction 90–92° under 2 mm. Subs., 0.7936, 0.7740: 32.6, 31.7 cc. of 0.1 N silver nitrate. Calcd. for $C_6H_9O_2I$: I, 52.88. Found: 52.14, 51.98.

The ester is soluble in the usual organic solvents except ligroin. It is *lacrymatory* and causes blisters on the skin.

Saponification of Ethyl 3-Iodocrotonate.—Twenty-five grams of ethyl 3-iodocrotonate (b. p. 90–92° at 2 mm.) was suspended in 250 cc. of 25% alcohol and was treated with 16 g. of finely powdered barium hydroxide below 0° as is described in the case of ethyl 3-chlorocrotonate under (c). After fifteen hours' stirring a sticky mass deposited in the flask; the solution was now decanted, 250 cc. of ether-saturated water added and the stirring continued for about five to six hours, etc., as usual. The yield was 8.5 g. of yellow crystals (m. p. 104–105°) from 250 cc. of ligroin (80–110°) or 53% of the theoretical. Recrystallization yielded 7.5 g. of yellowish crystals, m. p. 108°; a mixed melting point with 3-iodocrotonic acid (m. p. 108°) made from 3-chlorocrotonic acid was 108°. Seven grams of ester was recovered.

(2) 3-Iodocrotonic Acid.—To a cold solution of 40 g. of sodium iodide in 120 cc. of acetone, 24 g. of 3-chlorocrotonic acid (m. p. 83°) was added. In about half an hour the solution became clear. After one hour the sodium chloride was separated by filtration, etc., as in the case of ethyl 3-iodocrotonate; 11.2 g. of sodium chloride was separated (96%). From the crude crystalline residue of the ethereal solution (39.0 g.), 36.5 g. of yellow crystals (m. p. 108°) was obtained from ligroin (86%).

Anal. Subs., 0.2353, 0.6163: 11.05, 28.75 cc. of 0.1 N silver nitrate. Calcd. for $C_4H_5O_2I$: I, 59.8. Found: I, 59.6, 59.21.

The 3-iodocrotonic acid (m. p. 108–108.5°) crystallizes in yellow needles. It has approximately the same solubility as the 3-bromocrotonic acid. The compound is stable and may be stored for months.

IV. Reduction of 3-Chlorocrotonic Acid (m. p. 83°) with Palladium and Hydrogen

Two and four-tenths grams of 3-chlorocrotonic acid was dissolved in 20 cc. of water and cooled until much ice appeared in the solution; then 40 cc. of 1 *N* sodium hydroxide and 2.5 g. of palladium–norit (0.05 g. of Pd) was added and the mixture violently shaken in a hydrogen atmosphere. When approximately 460–480 cc. of hydrogen was consumed in the reduction (the hydrogen necessary for the saturation of palladium–norit must be taken into account), the solution contained the theoretical amount of sodium chloride and the reduction was interrupted immediately (the reduction does not stop at this point but would have gone further to the complete saturation of the compound). The products of three experiments were united and the palladium–norit was separated by filtration. The filtrate contained according to analysis the theoretical amount of sodium chloride and 4.8 g. of crotonic acid. The solution was now acidified with sulfuric acid and extracted with ether, etc. The residue of the ethereal solution was dissolved in low-boiling ligroin and the residue from this weighed 4.9 g. and was a semi-crystalline mass (95% of the theoretical). From this, 1.9 g. of recrystallized product (m. p. 71°) was obtained from low-boiling ligroin; a mixed m. p. with crotonic acid (m. p. 71.5°) was 71.5".

Reduction of 3,3-Dichlorocrotonic Acid.—Nine and three-tenths grams of 3,3-dichlorocrotonic acid (m. p. 42–43°) was dissolved in 180 cc. of 1 N sodium hydroxide at −3°. Then 1.6 g. of palladium–norit was added and the mixture violently shaken in a hydrogen atmosphere. The reaction was controlled by titration for chloride and for acidity. In about six hours, when about 1500 cc. of hydrogen was taken up, the amount of sodium chloride corresponded exactly to one mol and the titration for acidity showed that one mol of sodium hydroxide was neutralized. The reaction mixture was now worked up as before in the case of the reduction of 3-chlorocrotonic acid. The residue of the ligroin solution was 7 g. of yellow sirup, which deposited about 2 g. of crystals from low-boiling ligroin at −15°. The crystals after recrystallization from ligroin melted at 58–60°; from water also at 58–60°.

Three and four-tenths grams of the mother liquor of the crystals was dissolved in 10 cc. of a saturated solution of sodium iodide in acetone and the solution was allowed to stand for twenty-four hours. The sodium chloride was separated by filtration, etc., as usual. Two-tenths gram of sodium chloride was obtained. The ethereal filtrate gave 0.1 g. of yellow crystals (m. p. 108"); a mixed melting point with pure 3-iodocrotonic acid gave 108°.

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Summary

1. An improved method of preparation of 3-chlorocrotonic acid (m. p. 83°) is reported. The acid is prepared from 2-hydroxy-3-chloro-n-butyronitrile in the following manner. The nitrile is esterified in absolute alcohol with hydrogen chloride and the resulting ethyl 2-hydroxy-3-chlorobutyrate is treated with phosphorus pentoxide. The ethyl 3-chlorocrotonate thus obtained is saponified with alkali in order to obtain the 3-chlorocrotonic acid (m. p. 83°). The yield of this acid from the nitrile is 32% of the theoretical.

A new method for the preparation of 2-hydroxy-3-chlorobutyronitrile is reported which involves the treatment of dichlorohydrin with sodium cyanide in aqueous suspension.

It is shown that in the treatment of ethyl 2-hydroxy-3-chlorobutyrate with phosphorus pentoxide, two isomeric unsaturated esters are obtained. The main product is ethyl 3-chlorocrotonate; the by-product is very probably ethyl 3-chloro-vinylacetate.

Saponification of ethyl 3-chlorocrotonate with barium hydroxide below 0° is reported. The yield is as high as 85%.

2. The preparation of 3-bromocrotonic acid (m. p. 74°) is reported. This acid is prepared from 2-hydroxy-3-bromobutyronitrile in the same manner as in the case of 3-chlorocrotonic acid. The yield of acid, taking the nitrile as a basis, is about 12% of the theoretical.

A greatly improved method of preparation of dibromohydrin is reported. This product may be obtained now from glycerin with 54% yield.

The preparation of 2-hydroxy-3-bromobutyronitrile from dibromohydrin is described.

The preparation of ethyl 2-hydroxy-3-bromobutyrate (b. p. 94–96' at 2 mm.) and ethyl 3-bromocrotonate (b. p. 80° under 2 mm.) is reported.

3. The preparation of ethyl 3-iodocrotonate (b. p. 92–93' at 2 mm.) and that of the 3-iodo-crotonic acid (m. p. 108°) are described.

4. The structure of the 3-halogenocrotonic acids is proved. The 3-chloro acid may be reduced to crotonic acid (m. p. 72°); the 3-chloro- and 3-bromocrotonic acids may easily be converted into 3-iodocrotonic acid.

5. It is shown that the 3-chlorocrotonic acid is an intermediate product in the reduction of 3,3-dichlorocrotonic acid to crotonic acid.

6. An improved method of preparation of 3,3-dichlorocrotonic acid is described. The reduction of 3,3,3-trichlorocrotonic acid with zinc in acetic acid yields the 3,3-dichlorocrotonic acid in 80–85% yield.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

OXIDATION OF UNSATURATED COMPOUNDS. III. OXIDATION OF 3-CHLOROCROTONIC ACID. SYNTHESIS OF dl-THREONIC ACID. PROOF OF CONFIGURATION OF THE *dl*-1,2-DIHYDROXYBUTYRIC ACIDS

BY GÉZA BRAUN[1]

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In the study of hydroxylation of double bonds, undoubtedly fumaric and maleic acids have the most prominent place. Their structure was determined with a considerable degree of assurance[2] and the structure of their hydroxylated products—that of the tartaric acids—was proved with the greatest accuracy. Because the configurations of both starting and end products are known, it would be a comparatively simple matter to study the mechanism of the hydroxylation and the nature of the oxidizing agent in the oxidation of fumaric and maleic acids. Unfortunately these acids have a very inactive double bond. As a matter of fact it is possible to get satisfactory results only with the strongest hydroxylating agents,

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[2] Although there might be objections, it is generally accepted that fumaric acid is the "trans" and maleic acid is the "cis" form.

such as potassium permanganate, and with osmic acid-activated chlorates. With these reagents fumaric acid always yields racemic acid and maleic acid always gives mesotartaric acid. The other group of hydroxylating agents—which would yield the ethylene oxide derivatives as intermediate products and which would give the tartaric acids isomeric with those obtained in the chlorate oxidations—cannot be used successfully in the oxidation of fumaric and maleic acids. These agents are hypochlorous acid and peracids. The reaction of hypochlorous acid with these acids was completely cleared up by Kuhn and Ebel,[3] but the reaction is very complicated and there does not seem to be any general rule in the oxidation, and the peracids, such as perbenzoic and peracetic acids, etc., proved to be unsuitable for the oxidation of fumaric and maleic acids.[3,4] In contrast to this, another pair of unsaturated acids—crotonic and isocrotonic acids—may easily be oxidized in such a manner that each of the isomeric acids, by application of different oxidizing agents, gives both of the theoretically possible *dl*-1,2-dihydroxybutyric acids in high yields.[4] To use the results of these oxidations as a basis of comparison in the study of the hydroxylation of double bonds, it was necessary to prove the configuration of the *dl*-1,2-dihydroxybutyric acids only, because the structure of the crotonic acids is known from Auwers and Wissebach's work.[5]

The proof of configuration of *dl*-1,2-dihydroxybutyric acids is presented in this paper. The proof is accomplished by an indirect method and is based on the fact that the *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid may be converted into racemic acid through the intermediate formation of threonic acid; on the other hand, it may be reduced to the *dl*-1,2-dihydroxybutyric acid (m. p. 74–75"). This shows clearly that the *dl*-1,2-dihydroxybutyric acid (m. p. 74–75') has the same configuration as racemic acid and the other possible acid—the *dl*-1,2-dihydroxybutyric acid (m. p. 81.5°) —must have a configuration corresponding to mesotartaric acid.

I. Oxidation of 3-Chlorocrotonic Acid

The 3-chlorocrotonic acid may be prepared now in 32% yield from the 2-hydroxy-3-chlorobutyronitrile.[6] The acid can be oxidized with osmic acid-activated chlorates to *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid according to Hofmann's method,[7] modified by Milas and Terry.[8] The reaction proceeds just as well as in the case of fumaric or maleic acids. There is no change in the acidity during the oxidation; consequently no

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[3] Kuhn and Ebel, *Ber.*, 58, 925 (1926).

[4] Boeseken, *Rec. trau. chim.*, **45**, 838 (1926); Géza Braun, THIS JOURNAL, **51**, 228 (1929).

[5] Auwers and Wissebach, ***Ber.***, 56, 715 (1923)

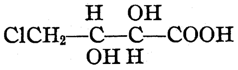
[6] Géza Braun, THIS JOURNAL, 52, 3167 (1930).

[7] Hofmann, Ehrhart and Schneider, *Ber.*, **46**, 1657 (1914).

[8] Milas and Terry, THIS JOURNAL, 47, 1412 (1925).

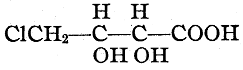
addition of hypochlorous acid to the double bond occurs as it does in the case of crotonic and isocrotonic acids.[4] As there is no formation of oxalic or volatile acids, it was concluded that no side reaction whatsoever occurred. The yield of oxidized, pure product (m. p. 97–98") is as high as 75–78% of the theoretical. The purest product melts at 100".

The analytical data indicate a formula $C_4H_7O_4Cl$. Considering the method of preparation of this compound, there are two possibilities for its structure



$ClCH_2-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-COOH$

I. *dl*-Threo-1,2-dihydroxy-3-chlorobutyric acid, or, briefly. 3-chlorothreonic acid



$ClCH_2-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-COOH$

II. *dl*-Erythro-1,2-dihydroxy-3-chlorobutyric acid, or 3-chloro-erythronic acid

Assuming that there is no inversion in the chlorate oxidations, the formula I would be expected to be correct. This was definitely proved by conversion of the compound into the racemic acid by oxidation with dilute nitric acid. Because the chloro compound cannot be oxidized directly, it was necessary first to remove the chlorine with silver acetate and then to oxidize the resulting product with nitric acid. The oxidation yielded, except for a small amount of oxalic acid, exclusively racemic tartaric acid. As the above reaction does not involve the asymmetric carbon atoms, no change in configuration can be assumed in this procedure and the oxidation definitely proves that the compound has the formula I.

The 3-chlorothreonic acid in all its reactions closely resembles the chlorohydroxy acids obtained from unsaturated acids by addition of hypochlorous acid. The organic chlorine is rapidly ionized in alkaline solution and the compound is converted into an ethylene oxide compound. In this case only one of the two asymmetric carbon atoms is involved in the reaction, whereas for instance in the case of the 1-chloro-2-hydroxybutyric acids the reaction takes place between both of the asymmetric carbon atoms. A comparison of these reactions offers interesting conclusions in regard to their mechanism. Work on these reactions is now in progress.

II. Synthesis of dl-Threonic Acid

Among the sugar acids that have been thoroughly studied only the *dl*-threonic acid has been unknown up to the present time. Nef[9] reported a mixture of dl-threonic and erythronic acids—obtained from 1-arabinose by alkali—but the pure dl-threonic acid could not be isolated.

The dl-threonic acid is prepared by treatment of *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid with silver oxide. According to this procedure the dl-threonic acid is obtained in 46% yield as a free acid (m. p. 98°). The acid according to analysis has a formula corresponding to $C_4H_8O_5$. Its configuration was proved by oxidation to racemic tartaric acid in the usual manner.

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[9] Nef, Ann., 357, 233 (1907).

Thus both of the theoretically possible dl-tetronic acids are known. The main difference between the two acids is that the dl-threonic acid does not form a lactone under the conditions in which the erythronic acid can be isolated only as a lactone. The characteristic derivatives of dl-threonic acid will be reported separately. The acid will be studied with special attention because of the fact that the 1-threonic acid, which was thoroughly investigated by Anderson,[10] was reported as a lactone.

III. Proof of Configuration of *dl*-1,2-Dihydroxybutyric Acids

As was mentioned before, the *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid has a prominent place as it makes a connection between the 1,2-dihydroxybutyric and the tartaric acids. After its configuration had been determined by conversion into racemic tartaric acid, it was only necessary to reduce the acid to one of the two theoretically possible 1,2-dihydroxybutyric acids in order to find which of these has the configuration corresponding to racemic acid.

The reduction was accomplished by palladium and hydrogen in the presence of alkali. The result of the reduction was the *dl*-1,2-dihydroxybutyric acid (m. p. 74°). Unfortunately the alkali causes a side reaction by formation of ethylene oxide compound, which lowers the yield of the desired product to about 50%, when all of the necessary sodium hydroxide is added at once. However, by gradual addition of sodium hydroxide during the reduction, it is possible to raise the yield of *dl*-1,2-dihydroxybutyric acid (m. p. 74°) to 70% of the theoretical. The reduction of the 3-chlorothreonic acid in acid solution has been thus far unsuccessful.

Bearing in mind that the result of reduction in alkaline solution is a *dl*-1,2-dihydroxybutyric acid, there are two possibilities for the course of the reaction: (1) the 3-chlorothreonic acid may be reduced directly to the dihydroxybutyric acid, or (2) the reduction may go through the ethylene oxide compound. In the latter case one of the asymmetric carbon atoms would be involved in the reaction and there would be a possibility of uncontrollable inversion, which would made the result indecisive. Although this is very improbable, a control reduction was made as follows: the 3-chlorothreonic acid was treated first with alkali in order to convert it into the ethylene oxide compound, and then this solution was added to an aqueous suspension of palladium on charcoal in a hydrogen atmosphere. The reduction proceeded in this case extremely slowly; the reaction mixture took up one molecule of hydrogen in about forty hours, whereas the direct reduction of the 3-chlorothreonic acid required only three to four hours. From the reduction product only about 15% of impure crystals of *dl*-1,2-dihydroxybutyric acid (m. p. 74°) was obtained, The great difference in the duration of the reduction and the quantity of acid obtained

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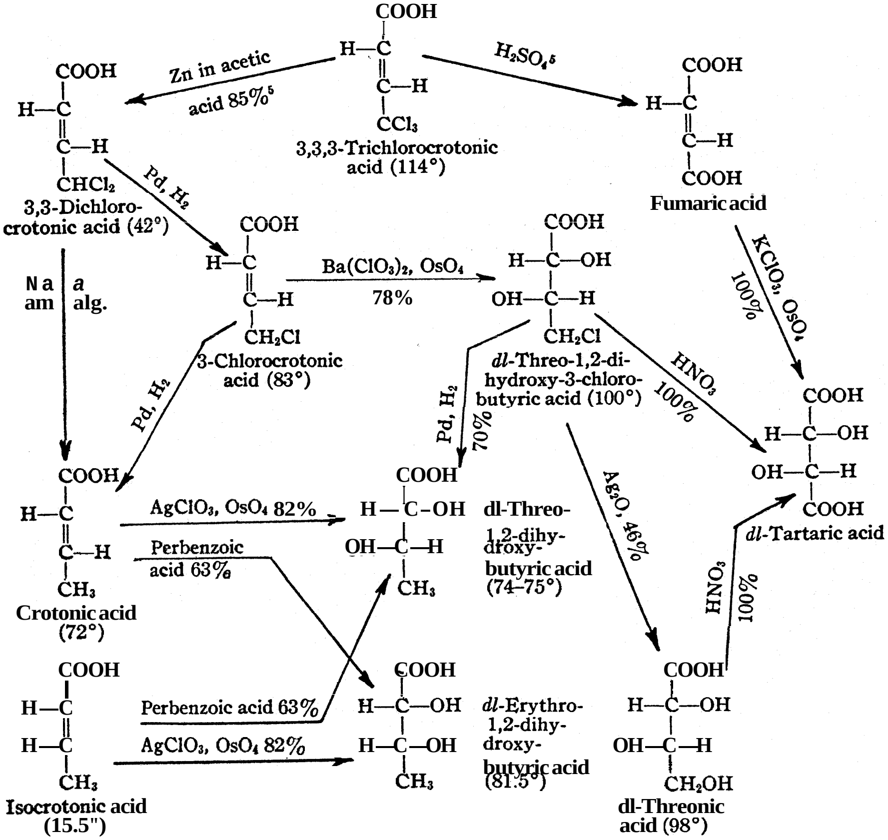
[10] Anderson, *Am. Chem. J.*, **42**, 425 (1909).

strongly supports the idea that Reaction 1 took place, and hence the asymmetric carbon atom was not involved in the reaction. It may be said, therefore, that the configuration of *dl*-1,2-dihydroxybutyric acid (m. p. 74°) corresponds to the racemic acid and that of *dl*-1,2-dihydroxybutyric acid (m. p. 81.5°) to the mesotartaric acid.

These results are a complete confirmation of the predictions made in a former publication.[4] In order to put an end to the last doubts on this subject, the reactions of 3-bromothreonic and 3-iodothreonic acids will be studied. These acids undoubtedly have much more active halogens and will be reducible in acid solution. Work on these reactions is in progress.

A general summary of all the reported reactions and the connection between the unsaturated and hydroxylated acids is shown in the chart.



Thus the structure of the *dl*-1,2-dihydroxybutyric acids having been established, the oxidation of crotonic and isocrotonic acids may be used as a basis of comparison in the study of hydroxylation of double bonds and especially for the study of the nature of any oxidizing agent. The final experimental data necessary to this purpose are supplied by the accomplishment of the separation of these acids from each other. The separation is based on the fact that the sodium salt of the "erythro" acid is about fifteen times as soluble in hot absolute alcohol as the corresponding salt of the "threo" acid. The separation is almost quantitative."

Experimental Part

Materials

Palladium Catalyst.—The catalyst was prepared by precipitating palladium on charcoal in the usual manner. The apparatus used in the reduction was a calibrated pyrex tube of suitable size which was connected with the reaction flask—a 250-cc. suction flask—and a leveling bulb. The reaction flask was connected with a dropping funnel and a Y-tube for the addition of any solution necessary during the reduction. The reaction flask was violently shaken on a shaking machine. For the neutralization of the organic and hydrochloric acids the purest sodium hydroxide (made from metallic sodium) was used. In this manner it was possible to use the palladium catalyst many times without any loss of catalytic power.

Oxidation of 3-Chlorocrotonic Acid.—One hundred and twenty grams of 3-chlorocrotonic acid (m. p. 81.5") was dissolved (partially suspended) in 1.5 liters of water which contained 0.5 g. of osmic acid and 60 g. of barium chlorate and the mixture was allowed to stand at room temperature. The mixture was frequently shaken at the beginning and cooled if the temperature rose over 30". In about four to five hours all of the acid went into solution and in twenty hours all of the chlorate was used up and the solution became black. Then 4 g. of chlorate was added and the solution again allowed to stand for eighteen hours. The clear solution was now extracted twice with 500 cc. of benzene and the aqueous solution concentrated at reduced pressure (temperature of the bath not over 50°) to a thin sirup, which was dissolved in absolute alcohol and the solvent again removed at reduced pressure until the residue became a thick sirup. This was dissolved in about 1.5 liters of ether, when all of the inorganic matter precipitated and the solution became clear. The ethereal solution was thoroughly dried with much sodium sulfate, etc., as usual. The residue of the ethereal filtrate was a thick, colorless sirup which soon crystallized to a semi-crystalline mass. This was dissolved in about 100 cc. of warm ethyl acetate and, after addition of 50 cc. of chloroform, cooled to −15°. The crystals were separated by filtration and washed with a cold mixture of 25% ethyl acetate and 75% chloroform (by volume). The mother liquor of the crystals was concentrated at reduced pressure and the crystallization was repeated as above. After three successive crystallizations there was obtained 109 g. of crystals (m. p. 97–98'). The residue was now dissolved in 500 cc. of ether, filtered and the residue of the ethereal filtrate dissolved in 75 cc. of ethyl acetate–chloroform mixture In two hours' standing at −15°, 7 g. of crystals was obtained making a total of 116 g or 75% of the theoretical.

When the oxidation was made with gradual addition of barium chlorate and the excess of the barium chlorate was reduced with sulfur dioxide, etc , just as in the case of the oxidation of crotonic acid with chlorates, the desired product was obtained in 78% yield. There was no change in the acidity during the oxidation.

The crude crystals were recrystallized from 250 cc. of hot ethyl acetate and yielded in two crops a total of 105 g. of crystals (m. p. 100°). The residue of the mother liquor was a crystalline mass.

Titration. Subs., 0.2870, 0.4308: 18.1, 27.4 cc. of 0.1 N alkali for free acid; 18.47, 27.5 cc. of 0.1 *N* alkali and 18.5, 27.5 cc. of 0.1 N silver nitrate for organically bound

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[11] Glattfeld and Braun, unpublished results.

chlorine after saponification on the water-bath for fifteen minutes. Calcd. for $C_4H_7O_4Cl$: mol. wt., 154.52; Cl, 22.95. Found: mol. wt., 158.6, 157.2; Cl, 22.85, 22.64.

Anal. Subs., 0.005875: CO_2, 0.006817; H_2O, 0.002388. Calcd. for $C_4H_7O_4Cl$: C, 31.06; H, 4.57. Found: C, 31.64; H, 4.55. Subs., 0.4223: 27.0 cc. of 0.1 *N* silver nitrate (after treatment with sodium in absolute alcohol). Calcd. for $C_4H_7O_4Cl$: Cl, 22.95. Found: Cl, 22.67.

The substance is very soluble in water, acetone, ether, hot ethyl acetate, etc., moderately soluble in cold ethyl acetate, insoluble in chloroform and benzene.

Oxidation of 3-Chlorothreonic Acid with Nitric Acid.—Three and one-tenth grams of the acid was dissolved in 50 cc. of water and after addition of 5 g. of silver acetate the mixture was heated for ten hours at 60° with frequent shaking. The filtrate from the silver chloride, from which the excess silver was quantitatively removed with hydrochloric acid, was concentrated at reduced pressure to a thick sirup. This was dissolved in 15 cc. of nitric acid (sp. gr. 1.21) and the solution kept at 55° for fifty-six hours. Then the nitric acid was removed at reduced pressure in the usual manner and the white crystalline residue dissolved in the necessary amount of 20% potassium hydroxide. After neutralization of this solution, 1.5 cc. of glacial acetic acid was added, whereupon the potassium acid tartrate crystallized immediately; 2.65 g. of crude crystals was obtained, which gave 2.1 g. of pure crystals (dried at 100") from 70 cc. of water.

Anal. Subs., 0.5036: 26.28 cc. of 0.1 N alkali. Calcd. mol. wt. for $C_4H_5O_6K$: 188.1. Found: 191.6.

0.5036 g. of potassium acid tartrate gave 0.66 g. of air-dried calcium tartrate.

Anal. Subs., 0.6570: loss in weight at 180°, 0.1812; ash, 0.1425. Calcd. for $C_4H_4O_6Ca\cdot 4H_2O$: H_2O, 27.70. Found: H_2O, 27.58. Calcd. for $C_4H_4O_6Ca$: CaO, 29.81. Found: CaO, 29.94.

The filtrate from the potassium acid tartrate was diluted to 200 cc. and the oxalic acid was precipitated with a small amount of calcium acetate in the hot; 0.2 g. of calcium oxalate was obtained.

Anal. Subs., 0.2079: CaO, 0.0803. Calcd. for $CaC_2O_4\cdot H_2O$: CaO, 38.34. Found: CaO, 38.62.

The filtrate from the calcium oxalate, after addition of more calcium acetate, deposited 0.3 g. of crystals; reprecipitated, 0.23 g.

Anal. Subs., 0.2245: loss in weight, 0.0605 (at 180°); ash, 0.0496. Calcd. for $C_4H_4O_6Ca\cdot 4H_2O$: H_2O, 27.70. Found: H_2O, 26.95. Calcd. for $C_4H_4O_6Ca$: CaO, 29.81. Pound: CaO, 30.2.

Treatment of 3-Chlorothreonic Acid with Silver Oxide; Preparation of dl-Threonic Acid.—Twenty grams of the 3-chlorothreonic acid was dissolved in 200 cc. of water and neutralized with barium carbonate at low temperature. After the carbon dioxide was removed at reduced pressure, the solution was filtered and in the course of about fifteen hours freshly precipitated silver oxide from 23 g. of silver nitrate was added very slowly at 30–35° while the solution was violently stirred. Then the precipitate was removed by filtration and the filtrate treated with silver oxide again until the solution did not contain any more organic chlorine. This was the case after about twenty hours' stirring. (The temperature at the end of the reaction was about 40°.) Then the barium and silver were quantitatively removed in the usual manner.

One tenth of the filtrate (corresponding to 2 g. of 3-chlorothreonic acid) was concentrated to dryness and the residue was oxidized with dilute nitric acid as previously described. One gram of pure recrystallized potassium acid tartrate, 0.24 g. of calcium oxalate and 0.18 g. of calcium racemate (27.25% H_2O, 30.5% CaO) were obtained.

No trace of mesotartaric acid was found, proving that the treatment with silver oxide did not cause any inversion.

The remaining portion of the filtrate (18 g. of 3-chlorothreonic acid) was concentrated to dryness and the residue dried for four hours under 2 mm. pressure at 40°. Thus 14.7 g. of colorless sirup was obtained. This sirup crystallized spontaneously in about twelve hours. It was found to be more practical to dissolve the sirup in 25 cc. of acetone before the crystallization and then seed the solution with the crystals. The crystallization started immediately: 7.15 g, of white crystals was obtained. Recrystallization from absolute alcohol yielded 3.1 g. of crystals (m. p. 98°).

Titration. Subs., 0.3000, 0.2054 (from different preparations): 20.45 (directly) +0.55 (after heating), 14.65 + 0.14 cc. of 0.1 N alkali. Calcd. for $C_4H_8O_5$: mol. wt., 136.06. Found: mol. wt., 142.8, 138.9.

Anal. Subs., 0.003876, 0.003884 (from different preparations): H_2O, 0.002094, 0.00205; CO_2, 0.005109, 0.00514. Calcd. for $C_4H_8O_4$: H, 5.93; C, 35.3. Found: H, 6.04, 5.90; C, 35.94, 36.1.

One gram of the crystals (m. p. 98°) was dissolved in 6 cc. of nitric acid (sp. gr. 1.21) and the solution kept at 56° for fifty hours, etc., as is described in the case of 3-chlorothreonic acid. The white, crystalline oxidation product gave 0.95 g. of recrystallized potassium acid tartrate.

Titration. Subs., 0.5200: 27.18 cc. of 0.1 *N* alkali. Calcd. mol. wt. for $C_4H_5O_6K$: 188.1. Found: mol. wt., 191.3.

Fifty-two hundredths of a gram of potassium acid tartrate gave 0.7 g. of calcium tartrate (air dried).

Anal. Subs., 0.6760: loss in weight at 180°, 0.1852; ash, 0.1468. Calcd. for $C_4H_4O_6Ca{\cdot}4H_2O$: H_2O, 27.70. Found: H_2O, 27.40. Calcd. for $C_4H_4O_6Ca$: CaO, 29.81. Found: CaO, 29.91.

The filtrate from the potassium acid tartrate gave 0.05 g. of calcium oxalate (CaO, 38.12; calcd., 38.34) and 0.07 g. of calcium tartrate (H_2O, 27.48; CaO, 30.03). No mesotartaric acid was found.

The dl-threonic acid was obtained therefore as a free acid (m. p. 98°). It is very soluble in water, in hot glacial acetic acid, in hot absolute alcohol; insoluble in acetone or ethyl acetate.

Reduction of 3-Chlorothreonic Acid with Palladium and Hydrogen. (a) Sodium Hydroxide Added in One Operation.—Three and one-tenth grams of 3-chlorothreonic acid was dissolved in 40 cc. of water and cooled in a freezing mixture until much ice appeared. Then gradually, under effective cooling, 40 cc. of 1 N sodium hydroxide and 5 g. of palladium–norit (corresponding to 0.1 g. of palladium) was added. The temperature during the neutralization should never rise above – 1°. Then the mixture was violently shaken in a hydrogen atmosphere. The operation must be carried out as quickly as possible and the temperature must be very low at the beginning. The reduction was practically complete in two hours but it was continued for four hours, when no more hydrogen was taken up. The reaction mixture took up approximately the theoretical amount of hydrogen (the hydrogen necessary for the saturation of palladium–norit—in this case about 180 cc.—must be taken into'account). The materials from three experiments were united (9.3 g. of 3-chlorothreonic acid); to the filtrate of the palladium–norit, which contained the theoretical amount of sodium chloride, 57 cc. of 1 N sulfuric acid was added and the solution concentrated to a thick sirup at reduced pressure. The residue was dried completely at 40° under 2 mm. pressure and extracted several times with hot ethyl acetate (altogether 250 cc.). The residue of ethyl acetate solution weighed 4.0 g. (55% of theoretical); this crystallized after considerable warming when the walls of the flask were scratched. The hard crystalline mass gave 3 g. of crystals (m. p. 73–74') from ethyl acetate. The mother liquor of these crystals deposited crystals again at 0°, showing the purity of the starting product. For identification see below under (b). The residue of the ethyl acetate extraction was treated with absolute alcohol. Three grams of a pale yellow sirup was obtained, which would not crystallize.

(b) Reduction with Gradual Addition of Sodium Hydroxide.—Three and one-tenth grams of 3-chlorothreonic acid was dissolved in 60 cc. of water, neutralized with 20 cc. of 1 N sodium hydroxide below 0° as under (a) and after addition of 10 g. of palladium–norit (0.2 g. of palladium) the mixture was violently shaken in hydrogen atmosphere in the apparatus previously described. After half an hour, when the solution was saturated with hydrogen, 22.5 cc. of 1 N sodium hydroxide was added very slowly in about three hours. The mixture was shaken for two hours further, when approximately the theoretical amount of hydrogen was taken up. The products of two experiments were united (6.2 g. of 3-chlorothreonic acid) as under (a). The residue of the ethyl acetate solution, which crystallized at once to a hard crystalline mass, weighed 3.4 g. (70% of the theoretical) dried over phosphorus pentoxide under 2 mm. pressure. From this, 2.9 g. of crystals (m. p. 74") was obtained in two crops (60% of the theoretical). The filtrate from the crystals (0.4) still deposited crystals.

A mixed melting point of the product with pure *dl*-1,2-dihydroxybutyric acid (m. p. 74–75°) was 74°.

One gram of this product was dissolved in 10 cc. of absolute alcohol and 0.9 cc of phenylhydrazine was added; 1.6 g. of hydrazide was obtained which yielded, after recrystallization from absolute alcohol, 1.25 g. of crystals (m. p. 132–133°); a mixed melting point with the phenylhydrazide of *dl*-1,2-dihydroxybutyric acid was 132–133".

Anal. Subs., 0.00456: N_2, 0.49 cc. (23.5°, 742 mm.). Calcd. for $C_{10}H_{14}O_3N_2 \cdot H_2O$: N, 12.28. Found: N, 12.30.

(c) Reduction of 3-Chlorothreonic Acid after Treatment with Sodium Hydroxide.—Three and one-tenth grams of 3-chlorothreonic acid was dissolved in 20 cc. of water and treated with 42 cc. of 1 N sodium hydroxide below 0° as described before. The solution was allowed to stand for three hours at −1°; then for two hours at room temperature. By this time 94–95% of the organic chlorine was ionized. This solution was now added to an aqueous suspension of 10 g. of palladium–norit (0.2 g. Pd)—which had been previously saturated with hydrogen—and the mixture was shaken in a hydrogen atmosphere. The theoretical amount of hydrogen (one mol) was taken up in about forty hours. The reaction mixture was worked up as under (a). The residue of ethyl acetate solution (1.6 g.) deposited impure crystals at —15" (about 0.6–0.7 g.) which gave 0.3 g. of crystals (m. p. 68°) from ethyl acetate. This product undoubtedly contained a large percentage of *dl*-1,2-dihydroxybutyric acid (m. p. 74°), formed by the reduction of unchanged 3-chlorothreonic acid which remained after the sodium hydroxide treatment.

The author wishes to thank Dr. J. Stieglitz for valuable suggestions, Dr. J. W. E. Glattfeld for help in the prosecution of this' work and the International Education Board for partial financial support.

Summary

1. The oxidation of 3-chlorocrotonic acid (m. p. 83°) with barium chlorate is reported. The oxidation yields the *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid (m. p. 100°) in 78% yield. The structure of the hy-

droxylated product is proved by conversion of the compound into the racemic tartaric acid in acid solution.

2. The treatment of the *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid with silver oxide gives the dl-threonic acid in 46% yield. It is shown that in this reaction no inversion occurs.

3. The preparation and properties of dl-threonic acid (m. p. 98°) are reported. The dl-threonic acid is a free acid and does not form a lactone under the conditions in which the dl-erythronic acid can be isolated only as a lactone.

4. The proof of configuration of the *dl*-1,2-dihydroxybutyric acids is reported. The proof is based on the fact that the *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid may be converted into racemic acid, and on the other hand it may be reduced to the *dl*-1,2-dihydroxybutyric acid, m. p. 74–75°, with a yield of 70%. This shows clearly that the *dl*-1,2-dihydroxybutyric acid, m. p. 74°, has the same configuration as racemic acid and the other possible acid—the *dl*-1,2-dihydroxybutyric acid m. p. 81.5"—has a configuration corresponding to mesotartaric acid.

The assignment of the prefixes "threo" and "erythro" which were previously suggested for the *dl*-1,2-dihydroxybutyric acids of melting points 74.5 and 81.5" respectively, is therefore justified.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

OXIDATION OF UNSATURATED COMPOUNDS. IV. OXIDATION OF CROTONIC ACID WITH HYPOCHLOROUS AND PERBENZOIC ACIDS

BY GÉZA BRAUN[1]

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The oxidation of crotonic acid with hypochlorous acid was first reported by Melikoff.[2] After the configuration of the dl-1,2-dihydroxybutyric acids had been established,[3] it was important to investigate Melikoff's work quantitatively. The oxidation of crotonic acid with hypochlorous acid to the *dl*-erythro-1,2-dihydroxybutyric acid (m. p. 81.5°) involves three operations: (a) addition of hypochlorous acid to crotonic acid, which yields the 1-chloro-2-hydroxybutyric acid; (b) treatment of 1-chloro-2-hydroxybutyric acid with alkali in order to obtain the 2-methylglycidic acid; (c) hydrolysis of 2-methylglycidic acid to the *dl*-1,2-dihydroxybutyric acid.

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[1] International Research Fellow in organic chemistry from Hungary, 1926–1928.

[2] Melikoff, *Ann.*, 234, 197 (1886); see also Glattfeld and Woodruff, THIS JOURNAL, 49, 2309 (1927).

[3] Géza Braun, *ibid.*, 52, 3176 (1930).

In the first operation (a) it was found that the reaction between the crotonic and hypochlorous acids may be indicated by the equation

$$CH_3CH{=}CHCOOH + Cl_2 + H_2O \longrightarrow CH_3CHOHCHClCOOH + HCl$$

The pure potassium salt of 1-chloro-2-hydroxybutyric acid was obtained from alcohol with 80% yield and the free acid, without isolation of a pure salt, with 30% yield.

The preparation of 2-methylglycidic acid (b) has been greatly improved and simplified. The pure acid (m. p. 88.5") was obtained from the crude reaction mixture in 64% yield.

The *dl*-erythro-1,2-dihydroxybutyric acid (m. p. 81.5°) *(c)* **was** obtained from the crotonic acid, without the isolation of the intermediate products, in 70–72% yield. The pure 2-methylglycidic acid (m. p. 88.5") hydrolyzes quantitatively to the above acid.

In order to obtain comparative results, the crotonic acid was oxidized with perbenzoic acid in non-aqueous solution. The result was the 2-methylglycidic acid (m. p. 88.5°) with about 20% yield. It was found therefore that the perbenzoic acid yields the same ethylene oxide compound that is obtained in the oxidation with hypochlorous acid.

The oxidation of pure isocrotonic acid with hypochlorous acid and the proof of configuration of the intermediate compounds is in progress.

Experimental Part

1. 1-Chloro-2-hydroxybutyric Acid.—Twenty grams of crotonic acid was dissolved in one liter of water which contained 500 g. of chopped ice. Then, under effective stirring and ice cooling, a slow stream of chlorine was conducted into the solution until absorption was complete (about three hours). The slight excess of chlorine was removed at reduced pressure in the cold.

(a) Potassium Salt of the Acid.—The solution was neutralized with **43** g. of potassium bicarbonate at 0° and the water removed at reduced pressure. The crystalline residue was washed with cold absolute alcohol and then treated with 150 cc. of hot alcohol. The filtrate from the potassium chloride deposited 15.5 g. of crystals after cooling; after addition of an equal volume of ether a further crystallization occurred (20.5 g.) making a total yield 36.0 g. of potassium salt or 80% of the theoretical. The salt contained only a trace of potassium chloride.

Anal. Subs., 0.4952: 2528 cc. of 0.1 N $AgNO_3$. Calcd. for $C_4H_6O_3KCl \cdot H_2O$: Cl, 18.22. Found: Cl, 18.13.

(b) Free Acid.—Another chlorinated solution of 20 g. of crotonic acid was neutralized with 43 g. of potassium bicarbonate and the solution concentrated at reduced pressure to small volume. After the neutral solution had been extracted with ether, the theoretical amount of dilute hydrochloric acid was added to the solution and the chlorohydroxybutyric acid thus freed extracted with ether, etc., as usual. The residue of the united ethereal solutions was 33.0 g. of a pale yellow sirup, which was dissolved in **10** cc. of ethyl acetate–carbon tetrachloride mixture, cooled to 0° and seeded. After ten hours' standing on ice the solution yielded 9.5 g. of crystals (m. p. 62-63°), or 30% of the theoretical (Melikoff's acid melted at 62–63'). The seeding crystals were obtained by letting the sirupy acid stand for several weeks in a desiccator.

2, 2-Methylglycidic Acid. (a) Potassium Salt.—To a chlorinated solution of

20 g. of crotonic acid an ice cold dilute solution of 45 g. of potassium hydroxide was added under stirring in the presence of much ice. The solution was then allowed to stand overnight at 0° and afterward for three to four hours at room temperature. The slight excess of potassium hydroxide was neutralized with hydrochloric acid, the solution distilled to dryness at reduced pressure, the residue dehydrated with absolute alcohol and treated with 100 cc. of hot absolute alcohol. To the filtrate from the potassium chloride 100 cc. of absolute ether was added, whereupon the potassium methylglycidate crystallized immediately (25.5 g.). From the mother liquor a second crop of 2.6 g. of crystals was obtained, making a total yield of 28.1 g. of crystals (dried over phosphorus pentoxide *in vacuo* to constant weight) or 86% of the theoretical. The crystals are very soluble in hot absolute alcohol and are very hygroscopic.

(b) Free Acid.—To the concentrated aqueous solution of potassium methylglycidate—prepared from three times 20 g. of crotonic acid as described above—the theoretical amount of dilute hydrochloric acid was added and the solution extracted several times with ether. The aqueous solution was further concentrated at reduced pressure and the solution was again extracted with ether. The residue of the united ethereal solutions weighed 69 g. and was a pale yellow sirup which crystallized immediately. This was dissolved in 15 cc. of warm ether and then 45 cc. of warm carbon tetrachloride was added and the solution was put on ice. The yield was 46 g. of crystals (m. p. 86°), or 64% of the theoretical. The crystals were dissolved in 45 cc. of hot carbon tetrachloride and 20 cc. of warm ether was added. The solution deposited in the course of several hours at room temperature 40 g. of crystals (m. p. 88.5°).

Titration. Subs., 0.3620: 34.34 cc. of 0.1 N alkali. Calcd. mol. wt. for $C_4H_6O_3$: 102.05. Found: 105.4.

Hydrolysis of 2-Methylglycidic Acid.—Four grams of acid (m. p. 88.5°) was dissolved in 200 cc. of water and allowed to stand for six weeks at room temperature. Then the water was removed at room temperature and the residue dried for several hours at 40°. The hard, crystalline residue weighed 4.6 g. or 97% of the theoretical; this gave 4.0 g. of crystals (m. p. 81.5–82°) from ethyl acetate; mixed m. p. with *dl*-erythro-1,2-dihydroxybutyric acid (m. p. 81.5°) obtained from crotonic acid with perbenzoic acid, 81.5°.

3. *dl*-Erythro-1,2-dihydroxybutyric Acid.—(a) A chlorinated solution of 20 g. of crotonic acid was treated with 45 g. of potassium hydroxide below 0° as is described under 2(a). The excess of potassium hydroxide was neutralized and then 80 g. of 10% hydrochloric acid was added and the solution kept at 98° for six hours in a water-bath. The water was removed at reduced pressure and the residue treated with ethyl acetate until no more precipitation occurred; the ethyl acetate solution was dried, filtered, etc. The yield was 24 g. of sirup, which gave 16.65 g. of crystals (m. p. 81°) or 60% of the theoretical; m. p. of the phenylhydrazide, 103°.

(b) From 20 g. of crotonic acid, 23.7 g. of crude 2-methylglycidic acid was prepared as described under 2(b), and dissolved in 2 liters of water. After six weeks' standing at room temperature, the solution was worked up in the usual manner. The yield was 25.4 g. of a pale yellow sirup which gave 19.8 g. of crystals (m. p. 80.5–81°) from ethyl acetate, or 71% of the theoretical.

Oxidation of Crotonic Acid with Perbenzoic Acid in Non-aqueous Solution.—Twenty grams of crotonic acid was dissolved in 280 cc. of dry chloroform which contained 43 g. of perbenzoic acid. After about three months' standing in a cool place only a small amount of peracid was present; the bromine titration showed about 8 g. of unchanged crotonic acid. The chloroform was then removed at reduced pressure, the residue treated with 250 cc. of water and the benzoic acid separated and washed with water. The aqueous solution was distilled to dryness at reduced pressure, the residue dissolved in water, the solution filtered and the filtrate again distilled to dryness. This operation was repeated several times in order to remove the benzoic and crotonic acids. The final residue was 10 g. of crystalline mass, which gave 4.7 g. of crystals (m. p. 88.5") from a mixture of ether and carbon tetrachloride, or 20% of the theoretical. A mixed m. p. with 2-methylglycidic acid (m. p. 88.5") obtained from crotonic acid with hypochlorous acid gave 88.5".

Anal. Subs., 0.008885: H_2O, 0.00479; CO_2: 0.01542. Calcd. for $C_4H_6O_3$: H, 5.93; C, 47.04. Found: H, 6.03; C, 47.33.

Summary

1. An improved method of oxidation of crotonic acid with hypochlorous acid is reported. The 1-chloro-2-hydroxybutyric acid (m. p. 62–63') is obtained in 30% yield, its potassium salt in 80% yield; the 2-methylglycidic acid (m. p. 88.5') in 64%, and its potassium salt in 86% yield. The hydrolysis of the crude 2-methylglycidic acid gives the *dl*-erythro-1,2-dihydroxybutyric acid (m. p. 81.5') in 60% yield at 100° and in 71% yield at room temperature.

2. It is shown that the 2-methylglycidic acid (m. p. 88.5') hydrolyzes in dilute aqueous solution quantitatively to dl-erythro-1,2-dihydroxybutyric acid (m. p. 81.5").

3. The oxidation of crotonic acid with perbenzoic acid in non-aqueous solution is reported. The oxidation yields the same 2-methylglycidic acid (m. p. 88.5") that is obtained from the crotonic acid with hypochlorous acid.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

OXIDATION OF UNSATURATED COMPOUNDS. V. STUDIES IN THE OXIDATION OF CONJUGATED SYSTEMS. OXIDATION OF PENTENOIC AND HEXENOIC ACIDS

BY GÉZA BRAUN[1]

RECEIVED NOVEMBER 27, 1929 PUBLISHED AUGUST 5, 1930

All the previous publications in this series were made preliminary to a systematic study of oxidation of conjugated systems. The investigation of vinylacrylic and sorbic acids was begun years ago. It was found that the vinylacrylic acid is easily oxidizable with hypochlorous acid but suffers partial decomposition in the oxidation with chlorates and perbenzoic acid. In contrast to this, sorbic acid is smoothly oxidizable with all these agents with good yield. The oxidation of sorbic acid with perbenzoic acid especially offers interesting results because it takes up the first molecule of peracid much more easily than the second, so there seems to be a possibility of a successful study of the mechanism of the oxidation.

But before this can be made it is necessary to study all the theoretically

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[1] International Research Fellow in organic chemistry from Hungary, 1926–1928.

possible valeric and caproic acids as well as the corresponding derivatives of the glycidic acid. With this idea in mind the preparation of all the theoretically possible *dl*-1,2-dihydroxyvaleric and caproic acids was accomplished by the oxidation of α,β-pentenoic and a,@-hexenoic acids. The oxidations were carried out in the same manner that was reported in the case of crotonic and isocrotonic acids.[2]

The a,@-pentenoicacid (m. p. 9.5–lo°) gave by oxidation with silver chlorate the *dl*-1,2-dihydroxyvaleric acid (m. p. 75°) with 80% yield, whereas with perbenzoic acid it yielded the *dl*-1,2-dihydroxyvaleric acid (m. p. 106°) with 75% yield.

The α,β-hexenoic acid (m. p. 33–34') gave with silver chlorate the *dl*-1,2-dihydroxycaproic acid (m. p. 108.5°) with 86% yield and with perbenzoic acid the *dl*-1,2-dihydroxycaproic acid (m. p. 99.5°) with 46% yield.

Proof of the configuration of these acids is in progress.

Experimental Part

Materials.——The α,β-pentenoic acid (m. p. 9.5") and the α,β-hexenoic acid (m. p. 34°) were prepared according to Doebner's method.[3]

Oxidation of α,β-Pentenoic Acid (m. p. 9.5°)

1. With Silver **Chlorate.**—Ten grams of pentenoic acid was dissolved in 500 cc. of water which contained 0.05 g. of osmic acid and 7.6 g. of silver chlorate was gradually added while the solution was kept in an ice-bath as described in the case of crotonic acid under III (B). The crude reaction product was 13.2 g. of a crystalline mass, which gave in two crops 10.7 *g.* of crystals (m. p. 75") from ethyl acetate or 80% of the theoretical. The m. p. of the product could not be changed by further crystallization.

Titration. Subs., 0.3824: 28.67 cc. of 0.1 *N* alkali. Calcd. mol. wt. for $C_5H_{10}O_4$: 134.08. Found: 133.4.

Anal. Subs., 0.00898: H_2O, 0.00613; CO_2, 0.01488. Calcd. for $C_5H_{10}O_4$: H, 7.52; C, 44.79. Found: H, 7.64; C, 45.19.

The acid has almost identical properties with the dl-threo-1.2-dihydroxybutyric acid, m. p. 74–75'.

Phenylhydrazide.—One gram of acid gave 1.4 g. of phenylhydrazide (m. p. 140.5°) from absolute alcohol. The salt is insoluble in cold absolute alcohol.

Anal. Subs., 0.00546: 0.551 cc. of N_2 (22°, 750 mm.). Calcd. for $C_{11}H_{16}O_3N_2 \cdot H_2O$: N, 11.57. Found: 11.52.

The substance partially loses its water of crystallization over phosphorus pentoxide ***in oacuo.***

2. With Perbenzoic Acid.—Ten grams of pentenoic acid was dissolved in 500 cc. of water and oxidized with 25 g. of perbenzoic acid in 125 cc, of chloroform under continuous shaking at 10° in the usual manner. The yield was 12.5 *g.* of sirup which gave 10.2 g. of crystals (m. p. 105–106°) from ethyl acetate or 75% of the theoretical. The recrystallized product melts at 106°.

Titration. Subs., 0.4114: 31.09 cc. of 0.1 N of alkali. Calcd. mol. wt. for $C_5H_{10}O_4$: 134.08. Found: 132.3.

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[2] Géza Braun, THIS JOURNAL, 51, 228 (1929).

[3] Auwers, ***Ann.,*** 432, 46 (1923); Goldberg, J. *Chem. Soc.*, 2343 (1928).

Anal. Subs., 0.009023: H_2O, 0.00616; CO_2, 0.01496. Calcd. for $C_5H_{10}O_4$: H, 7.52; C, 44.79. Found: H, 7.64; C, 45.21.

The acid has almost the same properties as the *dl*-erythro-1,2-dihydroxybutyric acid (m. p. 81.5").

Phenylhydrazide.—One gram of acid gave 0.75 g. of recrystallized phenylhydrazide (m. p. 119–119.5°) from absolute alcohol. The salt is moderately soluble in cold absolute alcohol.

Anal. Subs., 0.00431: N, 0.471 cc. (21.5°, 754 mm.). Calcd. for $C_{11}H_{16}O_3N_2$: N, 12.49. Found: N, 12.54.

Oxidation of α,β-Hexenoic Acid (m. p. 34")

1. With Silver Chlorate.—Twenty grams of acid was suspended (partially dissolved) in one liter of water and oxidized by gradual addition of 13.6 g. of silver chlorate in the presence of 0.1 g. of osmic acid at 0° in the usual manner. The yield was 25.2 g. of a crystalline mass which gave 22.6 g. of crystals (m. p. 108°) from ethyl acetate, or 86% of the theoretical. The residue from ethyl acetate crystallized again. The recrystallized product melted at 108.5".

Titration. Subs., 0.4354: 29.67 cc. of 0.1 N alkali. Calcd. mol. wt. for $C_6H_{12}O_4$: 148.1. Found: 146.7.

Anal. Subs., 0.009572: H_2O, 0.00693; CO_2, 0.0172. Calcd. for $C_6H_{12}O_4$: H, 8.17; C, 48.61. Found: H, 8.1; C, 49.00.

The acid was found to be very soluble in hot water and hot ethyl acetate, moderately soluble in cold water and ether, insoluble in chloroform.

Phenylhydrazide.—One gram of acid gave 1.5 g. of phenylhydrazide (m. p. 141.5–142°) from absolute alcohol. The salt is insoluble in cold absolute alcohol.

Anal. Subs., 0.00471: 0.450 cc. of N_2 (20.5°, 740 mm.). Calcd. for $C_{12}H_{18}O_3N_2 \cdot H_2O$: N, 10.93. Found: N, 10.82.

2. Perbenzoic Acid.—Ten grams of acid was dissolved in 125 cc. of chloroform. which contained 25 g. of peracid and after addition of 500 cc. of water the mixture was shaken at 10°, etc., as usual. The yield was 8.9 g. of a yellowish sirup which gave 6.0 g. of crystals (m. p. 98.5°) from ethyl acetate or 46% of the theoretical. The recrystallized product melted at 99.5°.

Titration. Subs., 0.3666: 24.95 cc. of 0.1 *N* alkali. Calcd. mol. wt. for $C_6H_{12}O_4$: 148.1. Found: 147.0.

Anal. Subs., 0.00884: H_2O, 0.00638; CO_2, 0.01586. Calcd. for $C_6H_{12}O_4$: H, 8.17; C, 48.61. Found: H, 8.08; C, 48.93.

The acid is very soluble in water, hot ethyl acetate and alcohol, moderately soluble in cold ethyl acetate or in ether, insoluble in chloroform.

Phenylhydrazide.—One gram of acid gave 0.75 g. of recrystallized phenylhydrazide (m. p. 120–121°) from absolute alcohol. The compound is moderately soluble in cold absolute alcohol.

Anal. Subs., 0.004367: N_2, 0.454 cc. (24°, 752 mm.). Calcd. for $C_{12}H_{18}O_3N_2$: N_2, 11.76. Found: N_2, 11.82.

Summary

The preparation of all the theoretically possible *dl*-1,2-dihydroxyvaleric and caproic acids is reported. The α,β-pentenoic acid (m. p. 9.5') gives by oxidation with silver chlorate the *dl*-1,2-dihydroxyvaleric acid (m. p. 75°) with 80% yield and with perbenzoic acid the *dl*-1,2-dihydroxyvaleric acid (m. p. 106°) with 75% yield.

The α,β-hexenoic acid (m. p. 33–34°) gives with silver chlorate the *dl*-1,2-dihydroxycaproic acid (m. p. 108.5°) with 86% yield and with perbenzoic acid the *dl*-1,2-dihydroxycaproic acid (m. p. 99.5°) with 46% yield.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

STRUCTURE OF THE CHLORALOSES. BETA-XYLOCHLORALOSE

BY L. D. GOODHUE, ANNE WHITE AND R. M. HIXON

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In a preceding paper[1] it has been shown that the available evidence indicates an acetal type of linkage for the union of chloral with glucose in β-glucochloralose rather than the carbon–carbon linkage depicted by the older formulas in the literature. The attempt to determine the configuration of the β-glucochloralose by means of methylation failed due to the resistance to hydrolysis of the partially dechlorinated trimethyl-β-glucochloralose.

In the literature[2] it has been shown that β-xylochloralose (formula III) yields chloralic acid (Formula II), which is identical with the acid obtained by oxidation of β-glucochloralose (Formula I), the formulas being used with the limitations of the preceding report.[1] The β-xylochloralose was accordingly drawn into these investigations in the hope that its greater range of solubility would make it possible completely to remove the chlorine, or on failure of this to hydrolyze the partially dechlorinated compound. Other than the chloralic acid,[2] the only definite derivative of β-xylochloralose reported in the literature is the dibenzoate.[3]

The β-xylochloralose was prepared according to the method of Hanriot. By further treatment with chloral hydrate and sulfuric acid, β-xylochloralose was converted to a crystalline dichloralxylose which could not be acetylated. This would indicate the absence of a free hydroxyl group in the dichloralxylose and could only be interpreted in terms of the acetal type of linkage as was the case with the conversion of β-glucochloralose to the dichloralglucoses. The possible Structures for the dichloralxylose would accordingly be analogous to the corresponding acetone derivatives reported by Freudenberg and Svanberg.[4] Experimental evidence indicates the existence of at least two isomeric dichloralxyloses.

Dimethyl β-xylochloralose was obtained by methylation of β-xylochloralose with dimethyl sulfate. Repeated methylations failed to increase the methoxy content above that for the di- derivative. Attempts to

[1] Coles, Goodhue and Hixon, THIS JOURNAL, 51, 519 (1929).

[2] Hanriot, *Compt. rend.*, 120, 153 (1895); 148, 487 (1909); *Bull. soc. chim.*, [4] 5, 819 (1909); *Ann. chim. phys.*, [8] 18, 466 (1909).

[3] Hanriot, *ibid.*, [8] 18, 466 (1909).

[4] Freudenberg and Svanberg, *Ber.*, 55, 3239 (1922).

acetylate the dimethyl-β-xylochloralose yielded a sirup whose chlorine analysis indicated slightly more acetylation than that required for mono-acetyl-dimethyl-β-xylochloralose. Acetylation of trimethyl-β-glucochloralose also gave a sirup whose chlorine analysis was within 1% of that calculated for the introduction of one acetyl group. These two compounds have not been obtained crystalline and are very difficult to distil, rendering further purification difficult.

The chlorines were partially removed from the dimethyl-β-xylochloralose by the use of sodium amalgam. It was not possible to obtain a preparation free from chlorine, and hydrolysis of the partially dechlorinated sirup introduced the same difficulties encountered with the corresponding glucose derivative. No attempt was made to isolate the intermediate dechlorinated compounds.

In working with the partially dechlorinated sirup, it was observed that alcoholic potassium hydroxide removed some of the chlorine. Hanriot and Kling[5] in working with the chloraloses were able to remove one chlorine atom by alcoholic ammonia but stronger alkalies were discarded because of the decomposition of the sugar molecule. Using β-glucochloralose, it has been found that refluxing with alcoholic potassium hydroxide yields a sirup very easily hydrolyzed by acids. The intermediate compound does not reduce Fehling's solution to any extent. The glucosazone is easily obtained after the acid hydrolysis.

Acetylation of β-xylochloralose by means of pyridine and acetic anhydride yields a beautifully crystalline diacetyl-β-xylochloralose. As Hanriot[2] reports, acetylation by means of acetyl chloride and zinc chloride yields an indefinite sirup. Distillation of this sirup in a high vacuum is accompanied by some decomposition. Chlorine analyses indicate a degree of acetylation greater than that of the diacetyl derivative.

A similar condition is encountered in acetylating β-glucochloralose. In the absence of zinc chloride, triacetyl-β-glucochloralose only is obtained. Refluxing with acetyl chloride and zinc chloride gives a mixture from which Hanriot[2] reports a tetra-acetyl-β-glucochloralose. Repeated fractional crystallization of this mixture yields the above triacetyl-β-glucochloralose, with a melting point (108°) which is almost identical with that reported by Hanriot for the tetra- derivative (106°). The analyses of the higher-melting compound (151°) correspond to a penta-acetyl-β-glucochloralose. Determinations of the acetyl groups by saponification are not possible, due to the above reported action of the alkali on the chlorines.

Repeated efforts have failed to give the tetra-acetyl-β-glucochloralose. The keto–enol isomerization postulated in the former paper[1] would not be necessary for the explanation of the tri- and penta-acetyl derivatives.

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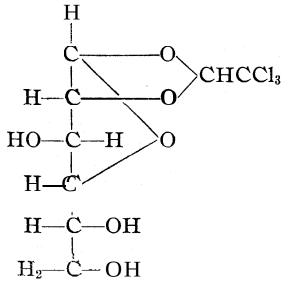
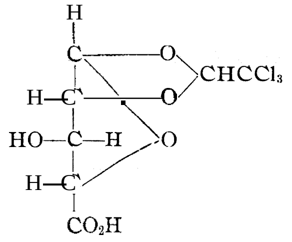
[5] Hanriot and Kling, Bull. *soc. chim.*, [4] 11, 207 (1912); *Compt. rend.*, 152, 1398 (1911).

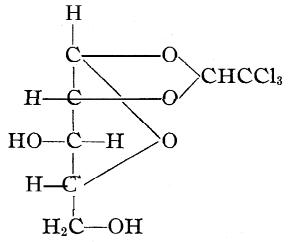
The triacetyl-β-glucochloralose would be formed by the acetylation of the free hydroxyl groups in the β-glucochloralose (Pormula I). The penta-acetyl-β-glucochloralose could be explained as due to the rupture of the oxide ring, as shown in Formula IV.



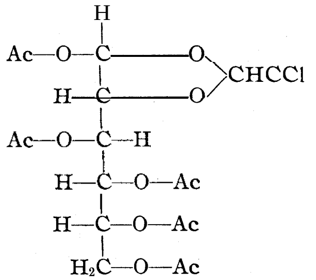
I. β-Glucochloralose



II. Chloralic acid



III. β-Xylochloralose



IV. Penta-acetyl-β-glucochloralose

Experimental Part

β-Xylochloralose was prepared according to the method of Hanriot. Attempts to isolate an or-xylochloralose in analogy with or-glucochloralosewere unsuccessful. It was found that the p-xylochloralose could be crystallized from hot benzene and from hot water. The yield was low, 100 g. of xylose giving only 60 g. of p-xylochloralose. The oxidation of the p-xylochloralose to chloralic acid identical with that from β-glucochloralose was repeated for confirmation. β-Xylochloralose is optically inactive in chloroform.

Preparation **of Dichloralxylose.**—The method is essentially the same as that used by Ross and Payne for the preparation of dichloralglucose. Fifty grams of xylose was stirred into a mixture of 200 cc. of sulfuric acid and 100 g. of chloral hydrate which was cooled to 12–15' under the tap. The mixture is allowed to come to room temperature and is stirred with a mechanical stirrer for six hours. The compound forms a rubber-like layer at the surface of the solution; transferred to cold water it was broken up to give a granular solid of lavender color. More compound is precipitated when the sulfuric acid mixture is poured into one liter of cold water. Heating the sulfuric acid solution to boiling precipitates about 10 g. of p-xylochloralose, which was crystallized in the usual manner from benzene. The combined portions of dichloralxylose were warmed with dilute sodium hydroxide solution until the excess of chloral was decomposed; yield, 90 g. of crude product. After repeated recrystallization from acetic acid and alcohol the melting point remained constant at 202". By treating β-xylochloralose as described above, the same crystalline dichloralxylose was obtained.

Anal. (Carius). Calcd. for $C_9H_8O_5Cl_6$: Cl, 52.08. Found: Cl, 52.15. 52.32.

The rotation in acetone (6.7 g. per 100 cc.) was $[\alpha]_D^{25}$ +25.2°.

Attempts to acetylate the compound with acetyl chloride and zinc chloride were without results. It is unchanged by dissolving in fuming nitric acid and allowing to stand for twenty-four hours. The compound is soluble in all common organic solvents.

Evaporation of the mother liquors used to recrystallize the above compound gave an oily sirup that will distil at 200° in a high vacuum to give a solid resin-like substance which softens at 100°. Analysis for chlorine is within 1% of that calculated for dichloralxylose. This is presumably an isomeric dichloralxylose.

Dimethyl-β-xylochloralose.—The method of preparation is essentially the same as that previously reported for the methylation of β-glucochloralose.[1] β-Xylochloralose is more soluble in dimethyl sulfate and is therefore more easily methylated. The product is sirupy, but is easily distilled at 135° under 2 mm. pressure. On long standing crystals form. They are oily and melt at about 53". Attempts to introduce another methyl group by repeated treatment with dimethyl sulfate and by the silver oxide method of Purdie and Irvine[6] were unsuccessful.

Anal. (Carius). Calcd. for $C_9H_{13}O_5Cl_3$: Cl, 34.60; MeO, 20.15. Found: Cl, 34.68, 34.70; MeO, 19.70, 19.65.

The rotation in chloroform (8.7 g. per 100 cc.) was $[\alpha]_D^{25}$ —41.08".

Reduction of **Dimethyl-p-xylochloralose** was carried out in a dilute alcoholic solution at 60° with sodium amalgam; 17 g. was treated in this manner for six days with 600 g. of 3% amalgam. The amalgam was added in small portions and the precipitate of sodium bicarbonate formed by passing in carbon dioxide was filtered off from time to time. At times the carbon dioxide was shut off and the mixture became strongly alkaline. Evaporation and extraction with ether gave 6–7 g. of a sirup boiling from 90 to 135" at 2 mm. pressure. The first fraction up to 115° gave an analysis for 5.5% chlorine. That calculated for one chlorine left in the molecule is 14.90. It reduced Fehling's solution on boiling.

The first fraction was hydrolyzed with 2 N hydrochloric acid and the aldehyde distilled out. Its water solution reduced Fehling's solution but the amount was too small to identify. An unsuccessful attempt was made to prepare a phenylhydrazine derivative of the sugar part of the molecule, the product forming a resin as does the methylglucose obtained from β-glucochloralose.

Action of Alkalies on **Chloralose.**—Seven grams of p-glucochloralose was refluxed for one-half hour with 50 cc. of alcoholic potassium hydroxide consisting of 25 cc. of a saturated solution of potassium hydroxide in 95% alcohol diluted with 25 cc. of alcohol. The alkali was partially neutralized and most of the alcohol evaporated under reduced pressure. Extraction with ether gave a compound that did not reduce Fehling's solution to any extent but which reduced very strongly after hydrolysis with dilute acid. An abundance of glucosazone separated after treatment with phenylhydrazine. The intermediate compound has not been obtained in a form suitable for analysis as yet.

Diacetyl-fi-xylochloralose was prepared by dissolving 8 g. of β-xylochloralose in 50 cc. of pyridine and adding 20 cc. of acetic anhydride. The mixture was stoppered and kept at 60° for three hours. About an equal volume of water is added, which causes the acetylated product to crystallize. It is filtered, washed with warm water and decolorized in alcohol with charcoal. The compound crystallizes as beautiful leaflets and after three recrystallizations melts sharply at 142°; yield, about 8 g.

Anal. (Carius). Calcd. for $C_{11}H_{13}O_7Cl_3$: Cl, 29.26. Found: Cl, 29.32, 29.43.

The rotation in chloroform (3.3 g. per 100 cc.) was $[\alpha]_D^{27}$ —7.61°.

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[6] Purdie and Irvine, J. *Chem. Soc.*, **83,** 1021 (1903); 85, 1049 (1904).

Triacetyl-β-glucochloralose was prepared from β-glucochloralose by the method given in the preceding paragraph for diacetyl-β-xylochloralose. It can also be prepared by treating β-glucochloralose with acetyl chloride without the addition of zinc chloride. It crystallizes well from dilute alcohol and melts at 108°.

Anal. (Carius). Calcd. for $C_{14}H_{17}O_9Cl_3$: Cl, 24.42. Found: Cl, 24.52, 24.64.

The rotation in chloroform (5.47 g. per 100 cc.) was $[\alpha]_D^{27}$ +22.72°.

Penta-acetyl-β-glucochloralose.—Fifteen grams of β-glucochloralose was refluxed for two hours with 100 cc. of acetyl chloride and 1 g. of zinc chloride. After evaporation of the acetyl chloride the sirup was dissolved in chloroform and extracted repeatedly with water. The chloroform was evaporated under reduced pressure and one volume of absolute alcohol added to the sirup. After long standing crystals form. The time required to crystallize the compound is much shortened if the solution is seeded.

Anal. (Carius). Calcd. for $C_{18}H_{22}O_{12}Cl_3$: C, 40.25; H, 4.13; Cl, 19.82. Found: C, 40.14, 40.05; H, 4.02, 4.12; Cl, 19.89, 19.90.

The rotation in chloroform (12 g. per 100 cc.) was $[\alpha]_D^{27}$ +46.12°.

If more than three acetyl groups can be introduced into the β-glucochloralose molecule, it would seem probable that trimethyl-β-glucochloralose could be acetylated. Trimethyl-β-glucochloralose is very markedly changed by treatment with acetyl chloride and zinc chloride but the resulting compound is a sirup that is very difficult to distil and so far has not been obtained sufficiently pure to warrant analysis.

Summary

1. Dichloralxylose was prepared from xylose and from β-xylochloralose.

2. Dimethyl and diacetyl derivatives of β-xylochloralose are reported.

3. Triacetyl and penta-acetyl-β-glucochloralose are described. The tetra-acetyl-β-glucochloralose reported by Hanriot could not be obtained.

4. The reactions of β-xylochloralose, like those of β-glucochloralose, indicate an acetal linkage between the sugar and chloral molecules.

5. Chlorine may be removed from β-glucochloralose by the action of alcoholic potassium hydroxide without decomposition of the molecule. The glucose can then be regenerated by dilute acids and identified as the osazone. The intermediate compound has not been isolated sufficiently pure for analysis.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

SKRAUP'S REACTION WITH PARA-AMINORESORCIN DIMETHYL ETHER

BY KONOMU MATSUMURA

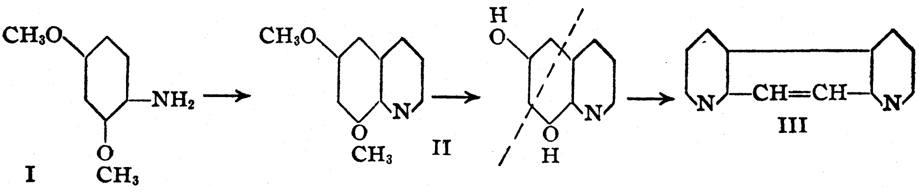
RECEIVED JANUARY 6, 1930 PUBLISHED AUGUST 5, 1930

In the course of the study upon the physiological action of certain quinoline compounds, I attempted the synthesis of 6,8-dimethoxyquinoline.[1] For this purpose, *p*-aminoresorcin dimethyl ether was submitted to the Skraup reaction for quinoline synthesis, and a small amount of crystals was isolated by means of benzene. It, however, could neither be a derivative of 6-methoxyquinoline nor any compound having any phenolic hydroxyl substituent. After a further purification, it formed colorless needles, m. p. 173°, being in coincidence with that of p-phenanthroline (6,8-dimethoxyquinoline has been reported to melt at 56°).[1]

From the analytical figures and the determination of molecular weight, the molecule formula $C_{12}H_8N_2$ could be assigned to it, and the characteristic constants of several derivatives of this compound were found to be generally in close agreement with the descriptions for those of *p*-phenanthroline given by the previous investigators.[2] Finally, the identification was fairly established by a mixed melting point with an authentic specimen of p-phenanthroline which had been prepared by a known method.

Experiments under a variety of conditions to obtain 6,8-dimethoxyquinoline or 6,8-dihydroxyquinoline failed to reveal any of these compounds; moreover, the formation of p-phenanthroline also resulted when *p*-benzene-azo-resorcin dimethyl ether or *p*-benzene-azo-resorcin was subjected to the Skraup reaction, which will be reported in a subsequent paper.

This reaction might be explained on the assumption that quinoline compound (II) might have been formed at an intermediate stage and that it might, at the instant of its formation, undergo ring rupture at the indicated place, followed by the condensation of two moles of such a compound, giving *p*-phenanthroline (III) in accordance with the equation



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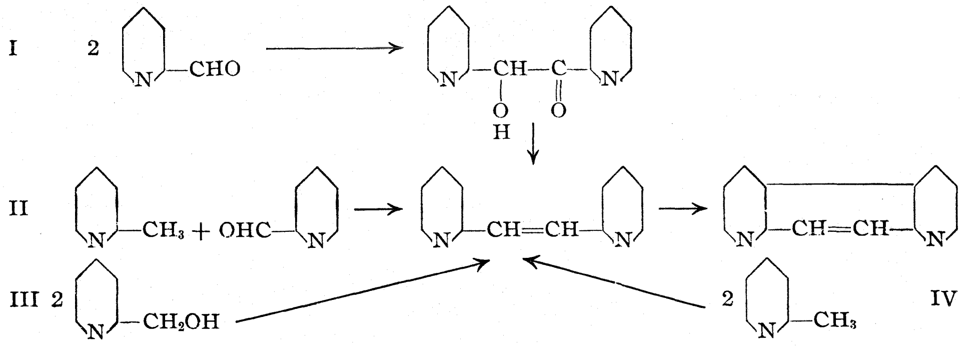
[1] During the investigation, the preparation of 6,8-dimethoxyquinoline through another course of synthesis has been reported by I. G. Farben Industry [*Chem.* Zentr., I, 2109 (1929); English Patent 301,9471.

[2] Skraup, Monatsh., 5, 569 (1884); Kaufmann, *Ber.*, 42, 2612 (1909).

If the suggested mechanism be admitted, concerning the final condensation, the following four possible courses which might be taken would be conceivable.



On subjecting benzoin to the Skraup reaction, benzil was formed in a good yield and a mixture of a-picoline and benzaldehyde, or a-picoline only, was also subjected to the Skraup reaction and in these cases a-picoline could be recovered without any notable loss. The possibility of the condensation through the course I, II or IV seems to be excluded by these experiments. On the other hand, the Skraup reaction with benzyl alcohol led to the formation of much resinous matter and neither stilbene nor phenanthrene could be isolated. This last failure appears also to rule out the course III, but recalling the fact that in case of a-methanol-pyridine the hydrogen atom in the side chain would be far more reactive than that of benzyl alcohol, in the case of pyridine series, therefore, such a condensation as through the course III might not be altogether impossible.

Experimental

Skraup's Reaction with ***p*-Aminoresorcin Dimethyl** Ether.—A mixture of *p*-aminoresorcin dimethyl ether (6 g.), glycerin (18 g.), arsenic acid (9 g.) and concd. sulfuric acid (18 g.) was refluxed on an oil-bath (bath temperature, 170–180°) for nine hours. The reaction mixture was digested with hot water and the filtered liquid, after being made alkaline, was shaken with benzene. On evaporating the solvent, 0.5 g. of colorless needles was obtained. It was best purified through a recrystallization of its sulfate from alcohol and a subsequent recrystallization of the free base regenerated from benzene in the presence of animal charcoal. It formed colorless needles melting at 173". It is easily soluble in alcohol and hot water, moderately in benzene and chloroform and rather difficultly in ether. The alcoholic solution, in case of only a concentrated solution, gives *a* reddish-brown color with ferric chloride. The absorption spectra of its 1/10,000 molar alcoholic solution shows the maximum absorption at 2696 Å. The mixed melting point of this substance and *p*-phenanthroline showed no depression.

Anal. (Water of crystallization). Subs., 0.0930: H_2O, 0.0213. Calcd. for $C_{12}H_8N_2 \cdot 3H_2O$: H_2O, 23.08. Found: H_2O, 22.90. Mol. wt. Subs., 0.0542, in 12.6100 g. of C_6H_6: *At*, 0.130°. Subs., 0.374 mg., in 3.189 mg. of camphor: At, 25.1°. Calcd. for $C_{12}H_8N_2$: mol. wt. 180. Found: mol. wt. 165, 187.

Anal. Subs., **3.718** mg.: CO_2, **10.933;** H_2O, **1.556.** Subs., **4.656:** CO_2, **13.634;** H_2O, 1.983. Subs., **2.350:** N_2, **0.336** cc. (32°, **761.5** mm.). Subs., **0.0462:** N_2, **6.1** cc. (13.5°, **760 mm.**). Calcd. for $C_{12}H_8N_2$: **C, 80.00;** H, **4.44; N, 15.56.** Found: C, **80.02, 79.86;** H, 4.65, 4.73; N, **15.36; 15.55.**

TABLE I

CHARACTERISTIC CONSTANTS OF THE DERIVATIVES OF THE COMPOUND $C_{12}H_8N_2$

Derivative	Crystal form	M. p., °C.
Picrate	Yellow needles from acetone	**255–256**
Chloroplatinate	Orange-yellow needles	**>310**
Hydrochloride	Colorless prisms from alcohol	**>315**
Sulfate	Colorless prisms from alcohol	**233–234**
Chromate	Orange-yellow needles. Black tar at	**225–230**
Monomethyl iodide	Light yellow needles from water	**268–269**
Dimethyl iodide	Garnet colored prisms from water	**271**
β,β'-Dipyridyl-α,α'-dicarboxylic acid	Short columns	**215** (dec.)
Sulfate	Colorless prisms from alcohol	**218**

		Analytical data, %					
Formula		Calcd.	Found		Calcd.	Found	
$C_{12}H_8N_2·C_6H_3N_3O_7$	C,	52.81	52.59	H,	2.69	2.85	
				N,	17.11	17.18	17.07
$C_{12}H_8N_2·2HCl·PtCl_4$				Pt,	33.10	33.34	
$C_{12}H_8N_2·2HCl$				HCl,	28.83	29.09	
$C_{12}H_2N_2·H_2SO_4·H_2O$	H_2O,	6.08	6.17	H_2SO_4,	35.25	35.96	
$C_{12}H_8N_2·H_2Cr_2O_7·2·5H_2O$				Cr_2O_3,	34.31	34.41	
$C_{13}H_{14}N_2I·H_2O$	H_2O,	5.30	5.45	I,	39.42	39.01	
$C_{14}H_{14}N_2I_2·H_2O$	H_2O,	3.73	4.22	I,	54.77	54.62	
$C_{12}H_8O_4N_2$	C,	59.02	59.04	H,	3.28	3.56	
				N,	11.48	11.76	
$C_{12}H_8N_2O_4·H_2SO_4·2H_2O$	H_2O,	9.52	9.61	H_2SO_4	28.66	29.24	

I hereby desire to express my hearty thanks to Professor Hata for the interest which he has kindly taken in this work.

Summary

In the Skraup reaction with p-aminoresorcin dimethyl ether, the formation of *p*-phenanthroline has been established.

TOKYO, JAPAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

THE FORMATION OF A PHENAZINE COMPOUND FROM A DIPHENYL ETHER DERIVATIVE

BY KONOMU MATSUMURA

RECEIVED JANUARY 30, 1930 PUBLISHED AUGUST 5, 1930

I. Nitration of Diphenyl Ether.—On treating diphenyl ether with concentrated sulfuric acid and potassium nitrate in exactly the same manner as that described for the preparation of 2,4,8,10-tetranitrodiphenylmethane,[1] tetranitrodiphenyl ether (m. p. 195–197°) was obtained, as was expected, in 80% yield. The melting point and other properties of this substance are in close agreement with those of 2,4,8,10-tetranitrodiphenyl ether (m. p. 195°) which was prepared by C. Willgerodt by the reaction of potassium dinitrophenolate and chlorodinitrobenzene,[2] and differing from tetranitrodiphenyl ether (m. p. 216°) which was isolated by W. Borsche as a by-product when he prepared m-dinitrophenol from *m*-dinitrochlorobenzene.[3] The structure of this compound was further confirmed by the fact that on alkaline hydrolysis it gave 2,4-dinitrophenol in quantitative yield.

The nitration of diphenyl ether has been studied previously by Mailhe and Murat[4] and recently by Suter[5] but no satisfactory method of preparing this compound has been indicated.

II. Reduction of 2,4,8,10-Tetranitrodiphenyl Ether.—According to M. Schöpff, on reduction by stannous chloride and concentrated hydrochloric acid, 2,4,8,10-tetranitrobenzophenone gave 3,6-diamino-acridone in good yield.[6] This was also confirmed by the author.[7] In the hope of forming diaminophenoxazine in an analogous way, 2,4,8,10-tetranitrodiphenyl ether was reduced in exactly the same manner that was described for tetranitrobenzophenone. But this is not the case, and 2,4,8,10-tetraminodiphenyl ether, which was identified as such by its analysis, insolubility in caustic soda and the determination of molecular weight for its tetrabenzoyl derivative, was formed nearly exclusively, accompanied by a small quantity of a phenazine compound as a by-product. Special efforts to convert the tetraminodiphenyl ether to the corresponding phenoxazine compound were all fruitless.

To return to the problem of the phenazine compound, whose method of isolation will be given in the experimental part, this substance formed

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[1] Matsumura, THIS JOURNAL, 51, 815 (1929).

[2] Willgerodt, Ber., 13, 887 (1880).

[3] Borsche, *ibid.*, 50, 1349 (1917).

[4] Mailhe and Murat, *Compt. rend.*, 154, 715 (1912); Mailhe, *Bull. soc. chim.*, [IV] 11, 1011 (1912).

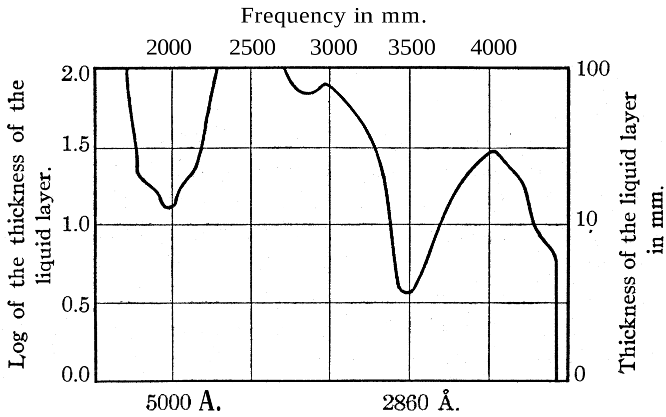
[5] Suter, THIS JOURNAL, 51, 2581 (1929).

[6] Schopff, *Ber.*, 27, 2318 (1894).

[7] Matsumura, THIS JOURNAL, 51, 815 (1929).

dark red crystals from alcohol, and it is characterized by a beautiful green color reaction with concd. sulfuric acid, this being a common color reaction of amino derivatives of phenazine compounds.

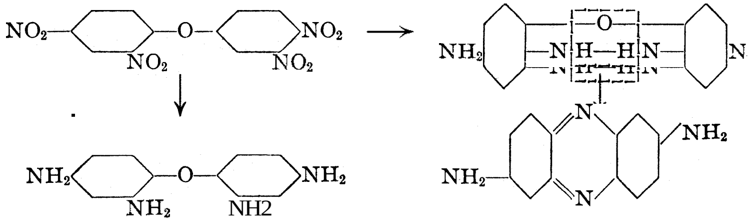
The analytical figures of this compound and its sulfate showed the compound to have a molecular formula agreeing with diaminophenazine. Finally, a phenazine base (m. p. 171°) was isolated from it by the diazo method, and the absorption maxima in visible and ultraviolet spectra were found to be in close agreement with those given for several amino derivatives of phenazine by F. Kehrmann and M. Sandoz[8] (Fig. 1 and Table I). From these facts, it may be concluded that the compound in question must be diaminophenazine.



1/10,000 mole alcoholic solution of diaminophenazine.

Fig. 1.

Concerning the problem of the positions of two amino groups, the following proposed interpretation for the mode of formation of this compound may serve in the solution of this problem. According to this explanation, the reaction involves formation of an intermediate seven-membered ring, dehydration and subsequent intramolecular rearrangement.



III

On the basis of this reaction, the substance must have the structure

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[8] Kehrmann and Sandoz, *Helv. Chim. Acta*, **3**, 109 (1920).

of 2,6 diaminophenazine (III), an unknown isomer of diaminophenazine.[9] A further fact of value in the elucidation of the structural problem is found in comparisons of the characteristic constants given by earlier investigators with the known phenazine compounds and those of the compound in question.

TABLE I

COMPARISON OF THE CONSTANTS OF PHENAZINE COMPOUNDS

Compound	Crystal	M. p., °C.	Absorption max. Visible spectra	Absorption max. Ultra-violet
3,6-Diaminophenazine	Dark yellow needles	280	447	265
2,3-Diaminophenazine	Brown-yellow needles	265	454	265–285
Author's diaminophenazine	Dark red columns	>320	506	285
2-Aminophenazine	Red needles	290–291	472	265

All compounds give a green color reaction with concd. sulfuric acid.

Experimental Part

2,4,8,10-Tetranitrodiphenyl Ether.—One hundred and thirty grams of finely powdered potassium nitrate was dissolved in 700 g. of concd. sulfuric acid below 30° during about three-quarters of an hour; 50 g. of diphenyl ether (m. p. 28–29°, b. p. 253°) was introduced into the solution under constant stirring during one and one-half hours at 10–25°. The mixture was then gradually warmed to 70° on the sand-bath and kept at that temperature for half an hour with stirring and then allowed to stand. After being cooled, it was poured into 5 liters of ice water, when a light yellow precipitate was obtained which was filtered and washed. After being dried, it was boiled with 200 cc. of alcohol, filtered while hot and recrystallized from 600 g. of boiling glacial acetic acid, giving small prisms of light yellow color; m. p. 195–197°; yield, 80 g. (about 80%) after recrystallization. After three further recrystallizations from glacial acetic acid, no change of melting point was seen.

Anal. Calcd. for $C_{12}H_6O_9N_4$: C, 41.14; H, 1.71; N, 16.00. Found: C, 40.92; H, 2.04; N, 16.05, 16.10.

Hydrolysis of 2,4,8,10-Tetranitrodiphenyl Ether.—A mixture of 2 g. of finely powdered 2,4,8,10-tetranitrodiphenyl ether and 50 g. of potassium hydroxide solution (20%) was heated at 100° for two hours. After being cooled, water was added and it was filtered from a small quantity of insoluble white prisms (0.4 g.), which was identified as the initial substance by its melting point (195–197°) and the mixed melting point method. On acidifying with dilute hydrochloric acid, the filtrate gave 1.1 g. of yellow flat prisms; m. p. 113–114°; 0.3 g. of an additional yield was obtained by shaking the mother liquor with ether. After one recrystallization from hot water, no change of melting point was seen. Its mixed melting point with 2,4-dinitrophenol (m. p. 111–112°) of Kahlbaum was 112–113°.

Anal. Calcd. for $C_6H_4O_5N_2$: N, 15.22. Found: N, 15.30.

Reduction of 2,4,8,10-Tetranitrodiphenyl Ether.—On the gradual addition of 35 g. of 2,4,8,10-tetranitrodiphenyl ether to the solution of 270 g. of stannous chloride in the same quantity of concd. hydrochloric acid (sp. gr. 1.9) at 100°, a vigorous reaction took place with spontaneous elevation of temperature to 115–120°, and the main reduction

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[9] The study of absorption spectra of sulfate of 2,6-diaminophenazine has been reported by Kehrmann, Ref. 8, but so far as I am aware the description of its synthesis has not been given in the literature.

appeared to be finished after a few minutes. The violet colored viscous fluid obtained was heated for a further half hour at the same temperature with a constant agitation. On being cooled, after the addition of water, tin was removed by repeated treatments with hydrogen sulfide. The earlier portion of the precipitates of tin sulfide assumed a violet color, on account of being admixed with phenazine compound (perhaps in the form of quinhydrone salt).

The filtered liquid, after being concentrated to a small volume under reduced pressure, was saturated with hydrogen chloride gas, when the liquid became filled with colorless crystals of the hydrochloride of tetraminodiphenyl ether.

The crystalline material was dried in a vacuum over sodium hydroxide; yield, 25 g. It forms colorless prisms and is extremely hygroscopic. It became light gray at 230° and dark violet at 280°, ammonium chloride subliming to the upper part. It does not melt at 310°. The aqueous solution, on the addition of ferric chloride, assumed a dark red color and afterward gave a dark brown precipitate. The aqueous solution, in contact with air, became brown after two days, and sooner on warming. The aqueous solution, on the addition of ammoniacal silver solution or gold chloride solution in the cold, gave precipitates of the corresponding metals. The aqueous solution, on the addition of concd. ammonia, assumed a beautiful blue color; the color faded after some time and brown precipitates appeared.

Anal. Calcd. for $C_{12}H_{14}ON_4 \cdot 4HCl$: Cl, 38.83. Found: Cl, 39.32.

The free base was best prepared in the following way. On the addition of an excess of caustic soda solution (10%) to 1 g. of the hydrochloride, in a separating funnel, light colored oil drops separated out. It was quickly shaken with a large quantity of chloroform. On concentrating the solvent, after drying with sodium sulfate, light brown crystals separated out. As it is extremely sensitive to air and alkali, treatment of more than 1 g. at a time is not desirable. It gives a colorless prism with light brown surface from benzene; m. p. 129°. The sample thus purified keeps well in the air for a long time. It is moderately soluble in hot chloroform, hot alcohol and hot benzene, but almost insoluble in ether, and somewhat soluble in cold water.

Anal. Calcd. for $C_{12}H_{14}ON_4$: C, 62.61; H, 6.09; N, 24.35. Found: C, 62.44; H, 6.40; N, 24.39.

2,4,8,10-Tetrabenzoylaminodiphenyl Ether.—To the solution of 1 g. of 2,4,8,10-tetraminodiphenyl ether hydrochloride in 10 g. of pyridine, 4 g. of benzoyl chloride was added gradually with stirring. After being allowed to cool, water was added and the solution acidified with dilute hydrochloric acid, when the reaction product separated in a colorless and resinous form. The water was decanted and the material repeatedly washed. The resinous matter, on repeated treatment with ether, turned to white crystals. It gives colorless needles from nitrobenzene; m. p. 232–233". It is easily soluble in hot chloroform, hot alcohol and cold acetone but **difficultly** in boiling benzene and almost insoluble in ether.

Anal. and mol. wt. Subs., 1.261 mg. in 9.445 mg. of camphor: *At,* 8.0°. Calcd. for $C_{40}H_{30}O_5N_4$: mol. wt., 646; C, 74.30; H, 4.64; N, 8.67. Found: mol. wt., 668; C, 74.68; H, 4.86; N, 8.84.

Various efforts to convert the tetraminodiphenyl ether to the corresponding oxazine compound were fruitless; for instance, (1) heating the hydrochloride alone or in the presence of fused zinc chloride in carbon dioxide atmosphere at 200" for twenty hours, or (2) heating it with glacial acetic acid at 140° for six hours, gave no definite substance, (3) heating it with hydrochloric acid (13%) at 160° appeared to have caused hydrolysis of the phenolic ether and gave, on further working, nothing but a black tar.

Diaminophenazine.—The first portion of the precipitate of tin sulfide which assumed a violet color, after thoroughly washing, was treated with an excess of caustic soda to complete dissolution of the tin sulfide, when a red substance remained undissolved. This was dissolved in dilute hydrochloric acid and the filtered bluish-violet solution, on making alkaline with ammonia, gave a dark red precipitate. It was recrystallized from alcohol; yield, 1.5 g. It forms hexagonal plates or columns of dark red color with a metallic luster. No change was seen at 320°. The absorption spectra of its 1/10,000 molar alcoholic solution is given in Fig. 1.

It is moderately soluble in boiling and cold alcohol, with orange-red color and yellow fluorescence, sparingly soluble in water and insoluble in benzene. It is fairly soluble in cold acetone with orange-yellow color and yellowish-green fluorescence, somewhat difficultly in warm chloroform with intense green fluorescence and sparingly soluble in ether with yellowish-green fluorescence. The solution in concd. sulfuric acid is bright green and on the addition of water becomes bluish-violet, and orange on the addition of a great excess of water. It dissolves in dilute hydrochloric acid with a purple-red color and on the addition of water the color becomes bluish-violet.

Anal. Calcd. for $C_{12}H_{10}N_4$: C, 68.57; H, 4.76; N, 26.67. Found: C, 68.60, 68.60; H, 4.84, 4.92; N, 26.24, 26.39.

Sulfate.—On addition of sulfuric acid (50%) to the alcoholic solution of the base violet needles of the sulfate ($C_{12}H_{10}N_4 \cdot H_2SO_4$) separate.

Anal. Calcd. for $C_{12}H_{10}N_4 \cdot H_2SO_4$: H_2SO_4, 31.82. Found: H_2SO_4, 32.35.

When it was recrystallized from hot water, after being allowed to stand for several days, large black-violet crystals of the sulfate ($(C_{12}H_{10}N_4)_2 \cdot H_2SO_4$) separated. The water of crystallization was removed at 130° in a vacuum.

Anal. Water of crystallization. Calcd. for $(C_{12}H_{10}N_4O_2)_2 \cdot H_2SO_4 \cdot 7.5H_2O$: H_2O, 20.67; C, 55.60; H, 4.63. Found: H_2O, 20.77; C, 55.83; H, 4.80.

Triacetyldiaminophenazine.—A mixture of 0.2 g. of diaminophenazine, 1.2 g. of acetic anhydride and 0.2 g. of fused sodium acetate was heated for two hours on the boiling water-bath. On cooling, water was added and the yellow crystals obtained were collected. It forms yellow prisms from alcohol; no change was observed at 320°. It is soluble in alcohol and acetone with yellow color and green fluorescence, very difficultly in hot chloroform, and almost insoluble in hot benzene and ether. The solution in concd. sulfuric acid is Bordeaux red; the color fades after a few minutes and a pure green color develops. Contrary to the expectation of obtaining a diacetyl compound, the analysis shows the presence of three acetyl groups.

Anal. Calcd. for $C_{18}H_{17}O_3N_4$: C, 64.09; N, 5.04; N, 16.62. Found: C, 64.14; H, 5.27; N, 16.92.

Phenazine.—On the gradual addition of an excess of finely powdered sodium nitrite to the cooled solution (−5°) of 0.4 g. of diaminophenazine in 24 g. of concd. sulfuric acid with vigorous agitation, the initial green solution became a dark violet, viscous mass. Then 120 cc. of alcohol was added and the clear brown solution obtained was refluxed for two hours on the water-bath. After evaporating the alcohol, the reaction mixture was made alkaline with caustic soda solution (25%) and shaken with ether. On evaporating the solvent, 0.2 g. of a yellow crystalline mass was obtained. It was sublimed in Kemp's apparatus under a diminished pressure; yield, 0.1 g. It gives yellow needles from alcohol, m. p. 170–171°. The solution in concd. sulfuric acid is blood red and on the addition of water becomes clear yellow.

Anal. Calcd. for $C_{12}H_8N_2$: N, 15.56. Found: N. 15.49.

I hereby desire to express my hearty thanks to Professor Hata for the interest which he has kindly taken in this work.

Summary

1. The preparation of 2,4,8,10-tetranitrodiphenyl ether by the nitration of diphenyl ether has been described.

2. In connection with the reduction of 2,4,8,10-tetranitrodiphenyl ether by stannous chloride and concd. hydrochloric acid, the formation of diaminophenazine and 2,4,8,10-tetraminodiphenyl ether has been observed.

TOKYO, JAPAN

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

SOME REACTIONS OF QUINOL AND A CONTRIBUTION TO THE CONSTITUTION OF QUINHYDRONE

BY THEODORE W. EVANS[1] AND WILLIAM M. DEHN

RECEIVED MARCH 1, 1930 PUBLISHED AUGUST 5, 1930

When an iodate reacts with quinol,[2] quite diverse effects are produced when the solutions are acid, neutral or alkaline. In general, quinhydrone or a dye or a mixture of these two is obtained.

In equal aqueous solutions the following products were obtained

Quinol, g.	$NaIO_3$, g.	CH_3COOH, g.	NaOH, g.	Product
10	6	5	0	7 g. of quinhydrone
10	6	0	0	9 g. of quinhydrone
10	6	0	5	Only the dye
40	25	0	0	39 g. of quinhydrone

Preparation of Quinhydrone.—The following is the most convenient and satisfactory method for the preparation of quinhydrone. To 40 g. of quinol suspended or dissolved in 200 cc. of water, add a cold saturated solution of 25 g. of sodium iodate. The mixture is shaken and kept cold by tap water. Almost immediately long glistening prisms begin to separate and in less than one-half hour a 90% yield and in 2–3 hours practically a quantitative yield can be filtered off as brassy black prisms melting at 171°. The reaction is in accordance with

$$6C_6H_6O_2 + 2NaIO_3 \longrightarrow 3C_6H_4O_2 \cdot C_6H_6O_2 + 2NaI + 6H_2O$$

Since hydriodic acid[3] reduces quinone to quinol, acid solutions give smaller yields.

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[1] The material presented in this paper is from part of a thesis submitted by Theodore W. Evans, du Pont fellow for 1929–1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1930.

[2] For the oxidation of quinol to oxalic acid, see Hesse, *Ann.*, **114**, 300 (1860); nitrogen oxides to nitranilic acid, Nietzki, *ibid.*, **215**, 138 (1883); silver sulfate and persulfuric acid to maleic and formic acid, Kempf, Ber., **39**, 3717, 3726 (1906); by other oxidants, Wohler, *Ann.*, **51**, 151 (1844).

[3] Wohler, Ref. 2. For the reaction of iodine in $KHCO_3$ solutions, see Valeur, *Ann. chim.*, [7] **21**, 529 (1900).

QUINHYDRONE BY OTHER OXIDATIONS

Oxidant	Quinol, g.	Yield of quinhydrone, etc , g.
29 g. $KMnO_4$ + 3.2 g. acetic acid	10	3
30 g. $K_3Fe(CN)_6$ + 5.5 g. KOH	10	6
5 g. $KClO_3$	10	0
13 g. $K_2S_2O_8$	10	9
10 g. $NaBO_3 \cdot 4H_2O$	10	Dye
20 g. $KBrO_3$	40	25

The persulfate[4] method gives beautiful crystals in practically quantitative yields, but requires many hours of standing for complete reaction. The bromate required one to two weeks to complete the reaction.

Quinone by the Iodate Method.—Varied conditions were employed and the mixtures were distilled with steam to separate the quinone.

Manner of treatment	Reactions	Yield of quinone,[5] %
Quinhydrone + $^1/_3$ mole $NaIO_3$	Neutral	41
Quinol to hot mole $NaIO_3$	Alkaline	0
Quinol to hot mole $NaIO_3$	Neutral	36
Quinol to hot mole $NaIO_3$	Neutral	40
$^1/_3$ Mole of $NaIO_3$ to hot quinol	Neutral	40

Here and elsewhere it is observed that alkaline solutions give little or no quinone; when alkaline oxidants react, a dye which yields a brown color on silk was formed. This dye can be salted from its solutions and is easily soluble in ammonium hydroxide. It will be investigated.

It is usually held that quinhydrone is first formed and is then completely oxidized to quinone. Whereas this is substantially true when aniline or quinhydrone is oxidized by chromate[6] solutions it was found that quinhydrone, by further oxidation with sodium iodate, did not yield additional quinone, but the quinol portion was oxidized to the dye. Since, on the one hand, numerous experiments with different aqueous reagents, even with water alone, directed to splitting quinhydrone into its constituent molecules, always gave less than 50% of quinone and no residual quinol but only the dye; and since, on the other hand, anhydrous solvents such as chloroform, toluene, etc., do produce dissociation into quinone and quinol, it seems that hot water and quinone have a profound effect on quinhydrone. These observations may bear upon the question of quinhydrone constitution. However, a more important contribution to this problem is the formation of the following compound.

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[4] Compare Kempf, *Ber.*, 39, 3717 (1906),

[5] Notwithstanding that only 40% yields are obtainable by the iodate method, it is very convenient for the preparation of quinone, since the materials need only be mixed and distilled with steam to obtain a pure product. The yields reported above did not include additional quinone which was contained in the aqueous filtrates.

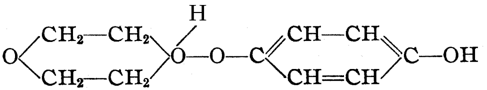
[6] Nietzki, *Ber.*, 19, 1468 (1886).

Quinoldioxane.—When 1–2 equivalents of dioxane are added to a saturated solution of quinol in dry ether, a precipitate of thick, transparent glistening rectangular plates, or the same with one, or with two opposite truncated corners, is formed.

Anal. Calcd. loss (of dioxane), when heated to 100°, from $C_6H_4(OH)_2 \cdot C_4H_4O_2$: 44.45. Found: loss, 44.48, 44.49.

The residue of quinol melted at 170°. Quinoldioxane melts in a sealed capillary at 93–100°. It is soluble in most organic solvents, difficultly soluble in chloroform and insoluble in petroleum ether, benzene and other hydrocarbons. A sample kept for six months in a stoppered vial lost 4%. It is soluble in water; such solutions precipitate quinhydrone when treated with quinol. A rapid method for the preparation of quinoldioxane is as follows. Dissolve quinol in a small volume of hot dioxane and then carefully add dry ether or petroleum ether.

Since all the atoms of dioxane are saturated, except its oxonium valencies, it seems very probable that Richter's formulas[7] as applied to the quinhydrones are the most valid. Thus quinoldioxane can be formulated



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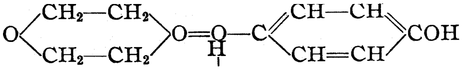

The second formula seems the more probable because the compound decomposes readily, and if these formulas are valid for quinoldioxane, then the analogous oxonium formulas depicted by Richter are the most probable for quinhydrone. Numerous experiments by the above method, with dioxane and phenols, amino derivatives, etc., to obtain other dioxane additive compounds were strictly negative; hence it is concluded that dioxane and quinol bear a unique structural or affinity relation in quinoldioxane, and it seems probable that a similar relation exists between quinol and quinone in quinhydrone. The uniqueness of this compound also makes it useful as an extremely characteristic test for quinol and dioxane.

Summary

Some new oxidations of quinol to quinhydrone and quinone are given. The additive compound of dioxane and quinol contributes to the theory of constitution of the quinhydrones.

SEATTLE, WASHINGTON

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[7] See *Ber.*, 43, 3603 (1910). For other formulas for quinhydrone see Wichelhaus, *ibid.*, 12, 1500 (1879); Jackson and Oenslager, *ibid.*, 28, 1614 (1895); Valeur, *Ann. chim.*, [7] 21, 560 (1900); Posner, *Ann.*, 336, 85 (1904); Urban, *Monatsh.*, 28, 299 (1907); Willstatter and Piccard, *Ber.*, 41, 1463 (1908).

[Contribution from the Insecticide Division, Bureau of Chemistry and Soils]

ROTENONE. VII. THE STRUCTURE OF TUBANOL AND TUBAIC ACID

By H. L. Haller and F. B. LaForge

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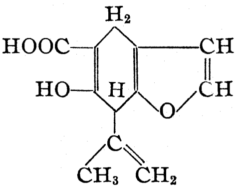
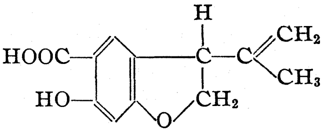
Tubaic acid, which corresponds to about half the rotenone molecule, is obtained from rotenone by the action of alcoholic potash. In recent articles, Takei, Koide and Miyajima[1] have proposed the tentative structural formulas I and II for this acid.



I

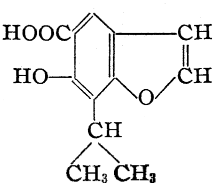


II

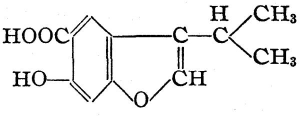
Butenandt and Hildebrandt[2] in a recent paper have also advanced arguments in favor of formula II.

In their latest communication[3] the Japanese investigators seem to prefer formula I, probably because an attempted synthesis[4] of a substance having the structure II did not meet with success. They state, however, that the position of the isoallyl (isopropylene) group may also be in the furan ring in which case this ring is hydrogenated.

Tubaic acid is converted by fusion with potassium hydroxide into an isomeric compound called rotenic acid for which Takei[1] has advanced the structural formulas III and IV. In formula IV also the isopropyl group is in the furan ring. Rotenic acid can also be prepared by fusing rotenone with solid potassium hydroxide, by dissolving tubaic acid in concentrated sulfuric acid and diluting the resulting solution with water, or by converting rotenone into isorotenone and then refluxing this compound with alcoholic potassium hydroxide solution.



III



IV

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[1] S. Takei and S. Miyajima, *Bull. Inst. Phys. Chem. Res.*, [8] 6, 61 (1929); S. Takei and M. Koide, *ibid.*, [8] 6, 64 (1929).

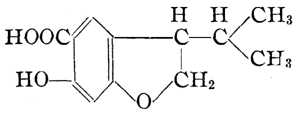
[2] A. Butenandt and F. Hildebrandt, *Ann.*, 477, 245 (1930).

[3] S. Takei and M. Koide, *Ber.*, 62, 3030 (1929).

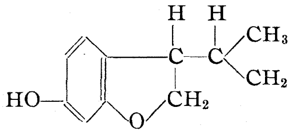
[4] Takei and Koide, *Bull. Inst. Phys. Chem. Res.*, [8] 6, 64 (1929).

Since rotenic acid can be obtained on isomerization of tubaic acid or from isorotenone, the change which takes place is the same in both cases. The difficulty with which isorotenone and rotenic acid are reduced catalytically leads to the conclusion that the isomerization is due to the shifting of a double bond, the mechanism of which is illustrated in the structures shown above.

A recent paper by Butenandt and Hildebrandt[2] presents some interesting experimental results on rotenone and its derivatives. They conclude from their data that structure II explains the properties of tubaic acid better than does structure I and that IV represents the structure of rotenic acid. They base their conclusion principally on the fact that they have succeeded in reducing rotenic acid to a dihydro derivative, V, and in resolving this compound into its enantiomorphs,[5] thus excluding the structural formula I for tubaic acid and III for rotenic acid since in these structures the dihydrorotenic acid would not possess an asymmetric carbon atom. Butenandt and Hildebrandt, probably inadvertently, have overlooked the fact that Takei has suggested that the isoallyl (isopropylene) group might also be in the furan ring.



V



VI

On being heated to 190–200° tubaic and rotenic acids give off carbon dioxide, and neutral substances result which are considered to be phenols by Takei and by Butenandt and Hildebrandt. Takei has named the compound derived from tubaic acid by the elimination of carbon dioxide tubanol and the corresponding compound from rotenic acid rotenol. The name rotenol had already been proposed by Butenandt[6] for the reduction product obtained by the action of zinc and potassium hydroxide on rotenone. It is very desirable that this original name be retained for Butenandt's product, but in this paper, in order to avoid confusion, we shall use the term "rotenol" to designate the compound obtained from rotenic acid. A new name for this compound is desirable.

Tubaic acid in alcoholic solution gives a violet color with ferric chloride, and rotenic acid produces an intensely blue color with this reagent. *Tubanol does not give a color with ferric chloride* whereas "rotenol" gives a violet-red color.[1]

Takei has proposed the structural formulas VII and VIII for tubanol

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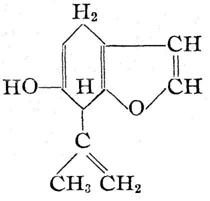
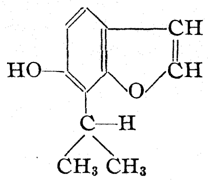
[5] Butenandt and Hildebrandt do not claim to have resolved the acid to its maximum nor has the dextro enantiomorph been resolved as much as the levo. The important point which has been established is that the compound *can* be resolved.

[6] A. Butenandt, **Ann., 464,253 (1928).**

and "rotenol," respectively. As in the case of tubaic and rotenic acids, the isoallyl and isopropyl groups may also be in the furan ring. The results of Butenandt and Hildebrandt, however, limit the position of the isoallyl and isopropyl groups to the furan ring.



VII



VIII

A substance having the structure of tubanol, VII, would be expected to give a color with ferric chloride, particularly since "rotenol," for which the structure VIII is advanced, produces a color. It is, of course, possible for the hydroxyl group to occupy one of four positions in the benzene ring if the side chain is in the furan ring. A compound, 2-methyl-5-hydroxycoumarone, which may be regarded as a lower homolog of one having the structure VIII but with the side chain in the furan ring, has been prepared by Karrer and Widmer.[7] It is a solid melting at 103° and in alcohol solution gives a brown-red color with ferric chloride which changes to blue on the addition of water. It polymerizes readily on the addition of dilute sulfuric acid. Rotenol is quite stable to dilute sulfuric acid and melts at 60°.

On reduction with sodium and alcohol 2-methyl-5-hydroxycoumarone gives 2-methyl-5-hydroxycoumarane, which is a lower homolog of a substance having the structural formula VI, the proposed structure of dihydro "rotenol." 2-Methyl-5-hydroxycoumarane is a solid melting at 96° and in alcohol solution produces only a slight change with ferric chloride, which on the addition of water changes to a pale yellow. "Rotenol" has not yet been reduced to dihydrorotenol, which should correspond to the isopropyl homolog of 2-methyl-5-hydroxycoumarane. If, as Butenandt and Hildebrandt seem to believe, dihydrotubaic and dihydrorotenic acids are identical, then it must follow that dihydrotubanol and dihydrorotenol are also identical. Dihydrotubanol prepared by Takei has a melting point of 59° and does not give a color with ferric chloride.

Rotenic acid is fairly stable on fusion with potassium hydroxide. Bergapten[8] and xanthotoxin[9] also contain the furan ring, but in these it is opened on fusion with alkali.

It has been generally assumed that the carboxylic acid group in tubaic acid arises from the ketone group present in rotenone and the hydroxyl

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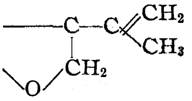
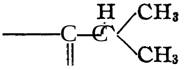
[7] P. Karrer and Fr. Widmer, *Helv. Chim. Acta*, 2,454 (1919).

[8] C. Pomeranz, *Monatsh.*, 12,379 (1891); 14, 29 (1893).

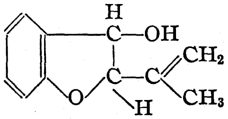
[9] H. Thoms, *Ber.*, 44,3325 (1911); 45,3705 (1912).

group is the result of the opening of the lactone ring. The lactone ring in rotenone is readily opened on catalytic hydrogenation to give an acid, whereas isorotenone in which the lactone ring is still present does not give an acid on catalytic hydrogenation. Furthermore, the double bond in rotenone which is readily reduced has disappeared in isorotenone. In the formula proposed by Takei and by Butenandt and Hildebrandt one would not expect any difference in behavior of the lactone ring on catalytic hydrogenation of rotenone and isorotenone.

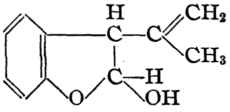
It seems reasonable to assume that the shifting of the double bond is responsible for the difference in behavior of the two lactones but if the OH group is assumed to be attached to the benzene ring as it is in the formulas of Takei and of Butenandt and Hildebrandt, this difference would not be expected.

If as stated above the other half of the rotenone molecule was joined through the hydroxyl group and the carbonyl group, it would give a substance having in its molecule a  group in rotenone and a  in isorotenone. Both types of groupings are very sensitive to sulfuric acid, giving rise to polymerization products. Rotenone is converted to isorotenone with sulfuric acid and isorotenone is very stable to sulfuric acid.

Also the fact that tubanol does not give a color with ferric chloride, and its stability toward sulfuric acid, lead us to believe that the structural formula IX or X more nearly represents all the known reactions of tubanol.



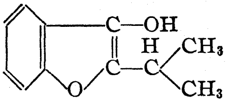
IX



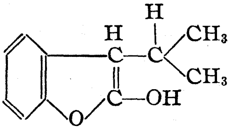
X

A substance having one of these two structures would not be expected to give a color test with ferric chloride, would be optically active and would be expected to be fairly stable toward sulfuric acid.

The structural formula XI or XII is proposed for "rotenol."



XI

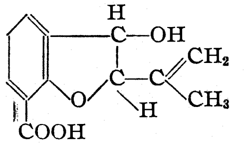


XII

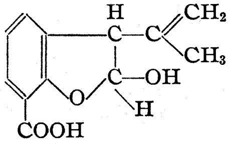
The questionable hydroxamic acid which Takei[10] obtained from rotenic acid methyl ether and hydroxylamine hydrochloride may be the oxime obtained by saponification of the methoxyl group and subsequent reaction with hydroxyl amine. Substances of the type XI react with hydroxylamine to give oximes.[11]

"Rotenol" gives a violet-red color with ferric chloride, which would be expected of a substance having the structure XI or XII.

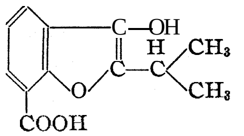
The structural formula XIII or XIV is proposed for tubaic acid, and XV or XVI is suggested for rotenic acid. These structures satisfactorily account for all the known facts. They would be expected to lose carbon dioxide readily on heating and their chemical behavior would be similar to that of tubanol and "rotenol." Attempts to synthesize some of these compounds are now under way.



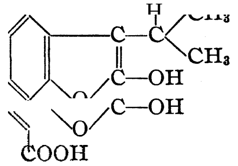
XIII



XIV



XV



XVI

In the course of our experimental work we have succeeded in simplifying the preparation of tubaic and rotenic acids and in improving the yields.

Experimental

Tubaic Acid.[12]—Ten grams of rotenone was added to a solution of 5 g. of potassium hydroxide in 100 cc. of 95% alcohol. The solution was refluxed in a boiling water-bath for three hours and then poured into 500 cc. of water. Carbon dioxide was passed into the turbid solution until precipitation was completed. The solution was filtered and allowed to stand at room temperature overnight. By morning usually another amorphous product had settled out. This was filtered off and the filtrate was acidified to congo red with 20% sulfuric acid. The resulting precipitate was filtered off and dissolved in ether. The filtrate was extracted three times with ether and the combined ether extracts were washed with water and then dried over anhydrous sodium sulfate. The ether was removed and the remaining tubaic acid was recrystallized from ether–petroleum ether. The yield was 1.5 g. Tubaic acid melts at 129° and when heated to 185–200° gives off carbon dioxide. In alcohol solution it gives a violet color with ferric chloride.

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[10] S. Takei, *Ber.*, 61, 1003 (1928).

[11] K. v. Auwers and W. Miiller, *ibid.*, 50, 1149 (1917).

[12] S. Takei (a) *Biochem. Z.*, 157, 1 (1925); (b) S. Takei and M. Koide, *Ber.*, 62, 3030 (1929).

Tubanol.—The procedure for the preparation of this compound was the same as that described by Takei.[12b] It is a thick viscous liquid: n_D^{20} 1.5623.

Rotenic Acid.—Rotenic acid was prepared from isorotenone by the same procedure employed in the preparation of tubaic acid. It melted at 186° with decomposition. In alcohol solution it gives an intensely blue color with ferric chloride.

Summary

An improved procedure for the preparation of tubaic and rotenic acids is given. Structural formulas are proposed for tubanol, "rotenol" and tubaic and rotenic acids.

WASHINGTON, D. C.

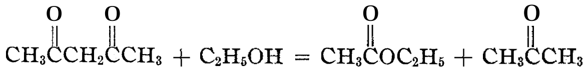
[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE ALCOHOLYSIS OF CERTAIN 1,3-DIKETONES IN THE PRESENCE OF HYDROGEN CHLORIDE

BY HOMER ADKINS, WALTER KUTZ AND DONALD D. COFFMAN

RECEIVED MARCH 11, 1930 PUBLISHED AUGUST 5, 1930

In the course of a study of the relationship of the constitution of the reactants to the point of equilibrium attained in the Claisen or acetoacetic ester condensation it seemed advisable to determine the rate of alcoholysis of a number of 1,3-diketones in the presence of hydrogen chloride. A typical reaction is as follows



$$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3 + C_2H_5OH = CH_3\overset{O}{\overset{\|}{C}}OC_2H_5 + CH_3\overset{O}{\overset{\|}{C}}CH_3 \qquad (1)$$

The alcoholysis of the diketones and analysis of the resultant solution for ethyl acetate were carried out as follows. Approximately 1×10^{-2} mole of the diketone was dissolved in dry ethanol, and a normal alcoholic solution of hydrogen chloride added so that the volume of the reaction mixture was 40 ml. and the desired amount of catalyst was present. If the amount of ethyl acetate expected in a reaction mixture was less than about 2×10^{-3} moles, the amounts of the reactants were increased so that at least that much ester would be present in the solution to be analyzed.

The reaction mixture contained in a 50-ml. tightly stoppered flask was placed in a thermostat and held at 60° for the desired length of time. The reaction was stopped by adding 2 ml. of phenylhydrazine. The mixture was then thoroughly shaken and cooled. The reaction flask, which bore on its side a Vigreux fractionating column 15 cm. in length, was then placed in an oil-bath whose temperature was slowly raised to 120° during the course of an hour or until the flask was dry. Three successive 10-ml. portions of dry ethanol were added to the residue in the flask and distilled out. The total time for the distillation was from two to three hours. An excess of an aqueous sodium hydroxide solution and a few drops of a phenolphthalein solution were added to the distillate and saponification allowed to proceed at 60° for three hours in a stoppered flask. The excess of alkali was then titrated and the amount of ester calculated. Determinations on samples containing from 1×10^{-3} to 1×10^{-2} mole of ethyl acetate showed that 1.5×10^{-4} mole of ethyl acetate was unaccounted for by the saponification value. This was presumably due to mechanical losses and saponification of the ester in the reaction flask before distillation. This correction was added to the amount of ester calculated from the saponification value. It was demonstrated that the recovery of ethyl acetate was the same irrespective of whether or not the mixture analyzed contained a monoketone, a diketone, other reaction products with phenylhydrazine, or an excess of phenylhydrazine. The above procedure was modified in those cases in which ethyl benzoate was to be determined. The distillation was then carried out at 16 mm. and three 10-ml. portions of tetrahydronaphthalene were used for boiling out the ester.

The rate of alcoholysis is, of course, a function of the temperature of the reaction mixture. In this investigation a temperature of 60° was selected as one at which alcoholysis proceeded at a reasonable rate, and one at which the vapor pressure of the alcoholic solution of hydrogen chloride was not large enough to complicate the experimentation. Another reason for avoiding higher temperatures is the probability of the reaction under such conditions of the ethanol and the hydrogen chloride.

The extent of alcoholysis of acetylbenzoylmethnne at the end of seventy hours was found to be 32% at 50°, 56% at 60° and 67% at 70° using a reaction mixture containing 9.85×10^{-3} moles of the diketone, 3.29×10^{-3} mole of hydrogen chloride and 40 ml. of ethanol.

It is necessary to have a rather high concentration of hydrogen chloride in order to secure a reasonably rapid rate of alcoholysis. In most of the experiments (see Figs. 2 and 3) described in this paper one mole of hydrogen chloride was used for three moles of the diketone. Even with this high concentration of catalyst more than four days were required for complete alcoholysis at 60° of diacetylmethane, the most reactive of the diketones studied. In Fig. 1 is shown the variation in the amount of alcoholysis of three diketones determined at the end of forty-eight hours, the ratio of diketone to hydrogen chloride being varied from 0.6:1 to 28:1. It may be seen that the reaction is practically complete within forty-eight hours in the presence of a molecular excess of hydrogen chloride, while with decreasing amounts of catalyst the amount of alcoholysis falls off rapidly to 10 or 20% of its former value.

A discussion of the role of the catalyst in the alcoholysis of 1,3-diketones will be reserved for a later paper, which will consider the alcoholysis in both acid and alkaline media, It should be pointed out at this time, however, that although the hydrogen chloride in all probability forms an addition compound with one or more of the reactants and is thus lost as a catalyst, it is still titratable as an acid and as a chloride, and in fact becomes active as a catalyst for alcoholysis if transferred to a fresh reaction mixture.

The condensation of an ester with a ketone does not occur to a detectable extent in the presence of hydrogen chloride, although this well-known Claisen or acetoacetic ester condensation does occur if sodium, sodamide or sodium ethoxide is present. The non-reversibility of the alcoholysis of five diketones was demonstrated for the reaction of ethyl acetate with acetone, methyl isopropyl ketone, methyl isobutyl ketone, methyl phenyl ketone and *n*-propyl phenyl ketone. This was done by making up mixtures of ethyl acetate, the monoketone, ethanol and hydrogen chloride and allowing them to stand at 60° for some days. The amount of ester determined by the method of analysis described above was always equivalent to that used in making up the mixtures.

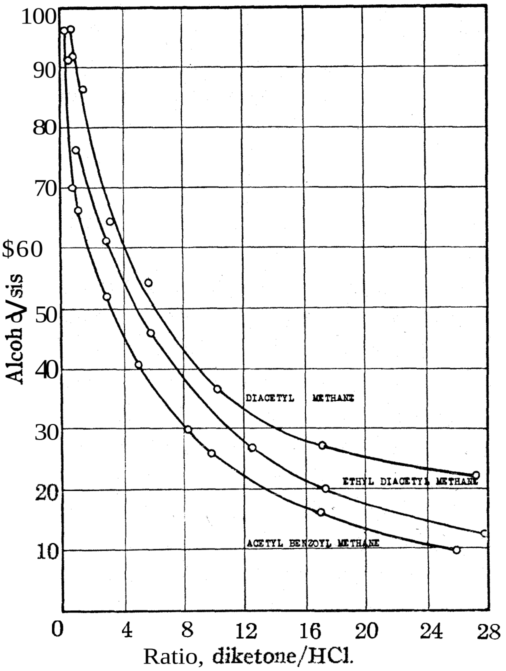
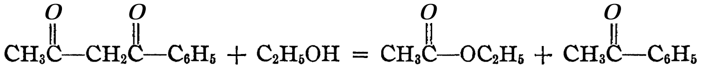


Fig. 1.—The percentage of alcoholysis of 9.8 × 10^{-3} moles of diacetylmethane, diacetylethylmethane and acetylbenzoylmethane in forty-eight hours at 60° in 40 ml. of ethanol is plotted against the moles of diketone per mole of hydrogen chloride in the reaction mixture.

The extent of alcoholysis for a given length of time was not a function of the ratio of diketone to alcohol when the ratio was varied from approximately 1:1 to 1:40. For example 1 × 10^{-2} mole of diacetylmethane was allowed to undergo alcoholysis for forty-eight hours at 60° in the presence of 3.6 × 10^{-3} mole of hydrogen chloride. The extent of alcoholysis was 19.0 to 19.2% for 4 × 10^{-1} mole of ethanol, 17.7 to 18.2% for 5 × 10^{-2} mole and 17.4 to 18.1% for 8.6 × 10^{-3} mole. In a similar fashion 1 × 10^{-2} mole of acetylbenzoylmethane with 1.4 × 10^{-3} mole of hydrogen chloride showed 31.8% alcoholysis with 4 × 10^{-1} mole of ethanol and 30.4% with 8.6 × 10^{-3} mole of alcohol. Thiophene-free benzene was added so that all reaction mixtures had a volume of 40 ml. An attempt was made to determine whether the extent of alcoholysis varied with different alcohols. It was found that under comparable conditions the extent of alcoholysis after forty-eight hours at 60° using 9.9 × 10^{-3} mole of diacetylmethane, 3.9 × 10^{-1} mole of ethanol and 3.6 × 10^{-4} mole of hydrogen chloride was 21.7%, while with butanol it was 20.8%. Tertiary butyl and isopropyl alcohols showed 11.1 and 18.3% alcoholysis, respectively, but this decrease in alcoholysis was no doubt due to the fact that 89% of the hydrogen chloride had reacted to form an alkyl chloride in the case of the tertiary alcohol, only 7% in the case of the secondary alcohol and to no measurable extent with the primary alcohols.

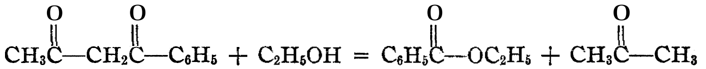
The rate of alcoholysis of the following list of diketones was investigated: diacetylmethane, ethyldiacetylmethane, n-propyldiacetylmethane, isopropyldiacetylmethane, n-butyldiacetylmethane, benzyldiacetylmethane, diethyldiacetylmethane, dibenzyldiacetylmethane, acetylbenzoylmethane, ethylacetylbenzoylmethane, isopropylacetylbenzoylmethane, benzylacetylbenzoylmethane and dibenzoylmethane.

Nine of these thirteen diketones contain two identical acyl groups in the same molecule, so that only one set of alcoholysis products are possible. On the other hand, such a diketone as acetylbenzoylmethane might give rise upon alcoholysis to two sets of products as shown in Equations 2 and 3, but fortunately the experimental work shows that only one pair of products is produced, Reaction 3 not taking place.



(2)

$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}{-}CH_2\overset{O}{\overset{\|}{C}}{-}C_6H_5 + C_2H_5OH = CH_3\overset{O}{\overset{\|}{C}}{-}OC_2H_5 + CH_3\overset{O}{\overset{\|}{C}}{-}C_6H_5} \qquad (2)$$



(3)

$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}{-}CH_2\overset{O}{\overset{\|}{C}}{-}C_6H_5 + C_2H_5OH = C_6H_5\overset{O}{\overset{\|}{C}}{-}OC_2H_5 + CH_3\overset{O}{\overset{\|}{C}}{-}CH_3} \qquad (3)$$

The fact that benzoylacetylmethane suffers decomposition according to Equation 2 and not at all according to Equation 3 was established by Dr. A. E. Broderick in the following manner. A mixture of 25 ml. of ethyl alcohol containing 1.6 × 10^{-2} mole of hydrogen chloride and 3.3 g. of acetylbenzoylmethane was placed in a pressure bottle and heated at 80° for thirteen hours. The mixture was then distilled and the alcoholic distillate saponified. The distillate showed a saponification number corresponding to 1.3 × 10^{-2} mole of ethyl acetate. The alcohol was removed by distillation, the residue of sodium salts was taken up in water, treated with sulfuric acid and a little potassium permanganate to oxidize the hydrogen chloride. This was distilled and a Duclaux determination made upon the distillate showed acetic acid to be present. Acetophenone was isolated and identified and the absence of acetone shown.

Benzylacetylbenzoylmethane in the presence of hydrogen chloride undergoes alcoholysis in a similar fashion, *i. e.*, the products of the reaction are ethyl acetate and benzylbenzoylmethane (benzylacetophenone). The diketone (2 × 10^{-2} mole) was refluxed with 1 × 10^{-2} mole of hydrogen chloride in 75 ml. of ethanol for fifty hours. The reaction mixture was then distilled on an oil-bath (120°) and 2 ml. of phenylhydrazine added to the distillate. This was then redistilled and yielded 6 × 10^{-3} mole of an ester. A Duclaux determination upon a solution of the acid from the ester gave values of 5.9, 6.4 and 6.0°; these indicate acetic acid. The residue from the first distillation was dissolved in 200 ml. of dry ether and treated with 2 × 10^{-2} mole of sodium ethoxide at 0°. The salt of the unchanged diketone precipitated out and was filtered off. After evaporating off the ether, the residue was refluxed for two hours with 5 × 10^{-2} mole of sodium hydroxide in a solution containing equal parts of water and alcohol. The alcohol was distilled off and the water solution extracted with ether. The ether extract yielded 1.3 g. of a ketone melting at 71–72° and its oxime melted at 80–81°. The ketone $C_6H_5CH_2CH_2COC_6H_5$ is reported to melt at 73° and its oxime at 82°.[1] Tests for the presence of benzoic acid gave negative results. Similar determinations upon the splitting of ethylacetylbenzoylmethane and of isopropylacetylbenzoylmethane were not made.

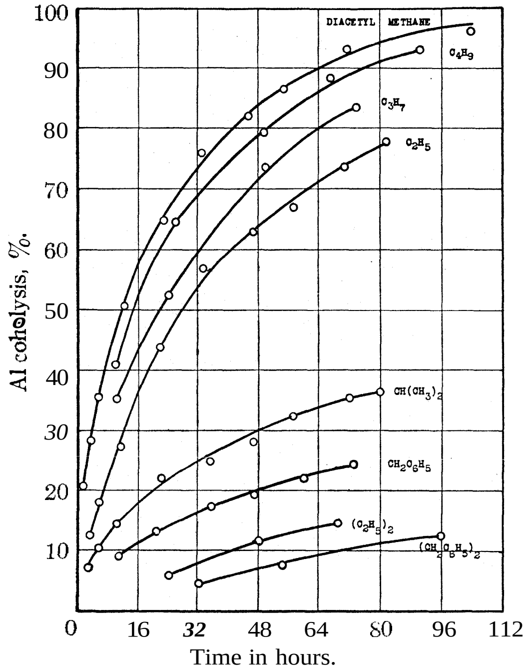


Fig. 2.—The percentage of alcoholysis of 1 × 10^{-2} mole of diacetylmethane and seven alkyl derivatives determined in the presence of 40 ml. of ethanol, and 3.33 × 10^{-3} moles of hydrogen chloride at 60° is plotted against the time in hours.

The relative rates of alcoholysis of diacetylmethane and seven of its derivatives in which substitution has been made on the methane carbon atom are shown in Fig. 2. These reactions were carried out at 60° in a reaction mixture containing the reactants in the ratio of 1 × 10^{-2} mole of the diketone, 3.3 × 10^{-3} mole of hydrogen chloride and 40 ml. of ethanol. A consideration of these data shows that substitution in the diketone decreases the rate of alcoholysis. Among the three purely aliphatic primary radicals the retarding effect decreases with the weight of the radical. The secondary propyl group is much more

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[1] "International Critical Tables," McGraw-Hill Book Co., New York City, 1926, Vol. I, p. 256; Perkin, *J. Chem. Soc.*, 59, 1007 (1891).

effective in retarding alcoholysis than is the normal group. The benzyl group is very effective and disubstitution even more so.

In Fig. 3 are shown the relative rates of alcoholysis of acetylbenzoylmethane and three of its derivatives. It is evident that the replacement of a methyl group in diacetylmethane by a phenyl group greatly reduces the rate of alcoholysis. However, the effects of substituting an ethyl, benzyl or isopropyl group in this unsymmetrical diketone are quite similar to their effects when substituted in diacetylmethane.

The alcoholysis of dibenzoylmethane was also studied but even when a molecular excess of hydrogen chloride was used the extent of alcoholysis was not greater than 7%. In view of the difficulties attendant upon the determination of such small quantities of ethyl benzoate as are here involved it is questionable whether the diketone undergoes an appreciable alcoholysis in the presence of hydrogen chloride at 60°. The stabilizing influence of one benzoyl group as in benzoylacetylmethane is very marked so that it is not surprising that a diketone containing two benzoyl groups should be quite stable to alcoholysis in the presence of hydrogen chloride.

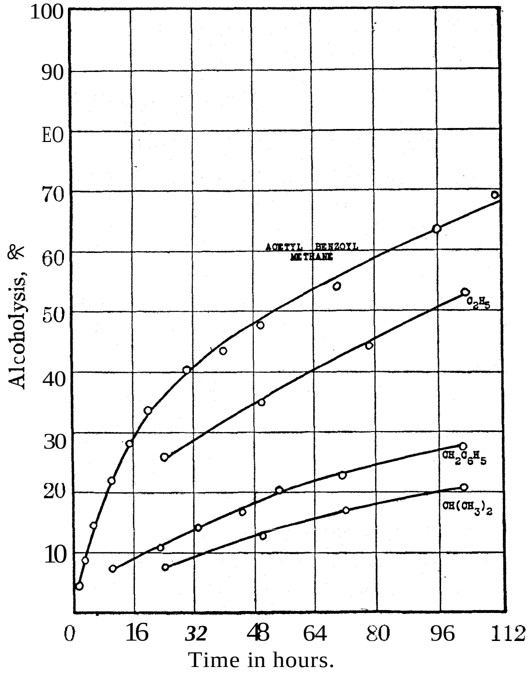

Fig. 3.—The percentage of alcoholysis of 1×10^{-2} mole of acetylbenzoylmethane and three alkyl derivatives determined in the presence of 40 ml. of ethanol and 3.33×10^{-3} mole of hydrogen chloride at 60° is plotted against the time in hours.

The significance of these facts in connection with the mechanism of alcoholysis of the diketones will be considered further in a forthcoming paper describing the result of an experimental study, already completed, upon alcoholysis of these same diketones in the presence of sodium ethoxide. It will suffice for the present to point out that the relative rates of alcoholysis in the presence of hydrogen chloride are roughly proportional to the extent of enolization of the diketones in an alcoholic solution.[2] Isopropyldiacetyl-

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[2] K. V. Auwers, *Ann.*, **415**, 169 (1918); K. H. Meyer, Ber., **45**, 2843 (1912); W. H. Perkin, *J. Chem. Soc.*, **61**, 800 (1892); Ida Smedley, *ibid.*, 97, 1493 (1910).

methane forms no copper salt,[3] gives no coloration with ferric chloride and shows a very slow rate of alcoholysis.

It is obvious from an inspection of the curves given in Figs. 2 and 3 that the reaction velocity "constant" is a steadily decreasing value. For example, in the case of diacetylmethane the constant calculated on the basis of a monomolecular reaction (since there is a great excess of alcohol) is at one hour 0.24, three hours 0.11, five hours 0.09. twelve hours 0.06 and at twenty-three hours 0.04. This is not suprising in view of the fact that the rate of alcoholysis had previously been shown to be independent of the concentration of alcohol and also in view of the high concentration of "catalyst" required.

Preparation of the Diketones

The substituted diacetylmethanes were prepared through the reaction in a glass or steel bomb of the monosodium salt of diacetylmethane with the proper alkyl halide. The sodium salt was prepared by adding diacetylmethane to the calculated amount of powdered sodium suspended in benzene or ether. The solid was filtered and used without purification.* The substituted acetylbenzoylmethanes were made in a similar manner. There is given in Table I for the preparation of each of the substituted diketones the following information: the amounts of reactants, the time and temperature for reaction, the yield, boiling range (or melting point) and density of the product, and the names of the authors who have reported the preparation of the compound under consideration. The analysis of the diketone not previously reported is given at the bottom of Table I.

Diacetylmethane was prepared by Claisen and Erhardt[5] through the condensation of ethyl acetate (3 moles) and acetone (1 mole) with sodium (1 mole) or with sodium ethoxide (1 mole). They reported a yield of 50% in the first case and 30 to 40% in the latter. Several runs were made in this Laboratory in which both catalysts were used in varying amounts. The result of this study indicated that the maximum yields for the two catalysts were the same and were obtained by using 2 moles of sodium or 1 mole of sodium ethoxide per mole of acetone. In this connection it is of interest to note that Claisen[6] reports the use of two moles of sodamide per mole of ketone and then compares the yield with that obtained when one mole of sodium and one mole of ketone were used.

A typical preparation was made as follows. A 5-liter, three-necked flask was fitted with a stirrer, a dropping funnel and an efficient condenser. Into the flask was poured 4 moles (92 g.) of sodium along with two or three hundred ml. of xylene. Twelve to fifteen hundred ml. of dry, alcohol-free ethyl acetate was now added and the flask immediately surrounded by a plentiful supply of ice. The stirrer was started and after ten or fifteen minutes dry acetone was added through the dropping funnel. Seventy ml. was added at once but no more added until it was certain that the reaction was under way. This was evidenced by the evolution of a large amount of heat and the separation

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[3] Morgan and Thomason, *J. Chem. Soc.*, *125*, 755 (1924).

[4] *Cf.* Combes, *Ann. chim. phys.*, [6] *12*, 207 (1887).

[5] Claisen and Erhardt, *Ber.*, 22, 1011 (1889).

[6] Claisen, *ibid.*, 38, 696 (1905).

TABLE I

PREPARATION AND PROPERTIES OF VARIOUS ALKYLATED DIKETONES

	Preparations1 reagents				
Alkyl halide	Moles	Sodium-( )-methane	Mole	Time, hours	Temp., °C.
Ethyl iodide	2.5	Diacetyl-	0.5	3	150
n-Propyl iodide	0.75	Diacetyl-	.25	12	150
Isopropyl iodide	2.0	Diacetyl-	.5	3	160
n-Butyl iodide	2.0	Diacetyl-	.5	3	180
Benzyl chloride	2.0	Diacetyl-	.5	12	180
Ethyl iodide	0.75	Ethyldiacetyl-	.2	10	150
Benzyl chloride	0.5	Benzyldiacetyl-	.1	10	250
Ethyl iodide	1.25	Acetylbenzoyl-	.3	6	145
Isopropyl iodide	0.75	Acetylbenzoyl-	.2	10	150
Benzyl chloride	2.0	Acetylbenzoyl-	.25	6	180

		Boiling point		
Methane compound	Yield, %	°C.	Mm.	d_{25}^{25}
Diacetylethyl-[7]	52	175–178	740	0.9365
Diacetylpropyl-[8]	30	192–194	740	.9328
Diacetylisopropyl-[8]	35	180–183	740	.9205
Diacetyl-*n*-butyl-[9]	38	90-94	10	.9312
Diacetylbenzyl[10]	48	155–160	5	1.0125
Diacetyldiethyl-[11]	32	95–100	10	0.9448
Diacetyldibenzyl-[10]	25	111–112 (melting point)		
Acetylbenzoylethyl-[12]	26	135–138	10	1.057
Acetylbenzoylisopropyl-[13]	12	146–149	10	1.043
Acetylbenzoylbenzyl-[14]	47	5556 (melting point)		

of a light yellow solid in the reaction mixture. After the reaction had slowed down the remainder of the acetone (total amount, 116 g., 2 moles) was added at such a rate that only a gentle refluxing took place. After the addition of the acetone the reaction mixture was stirred for two hours and then allowed to stand in a refrigerator for at least ten hours. The reaction mixture was poured into ice water with vigorous stirring and sufficient water added to dissolve the sodium salt completely. The upper layer of ethyl acetate and xylene was removed and the water layer acidified with glacial acetic acid. To this acid solution was added a concentrated ammoniacal aqueous solution containing 200 g. of copper acetate. The copper salt of the diketone separated at once. After standing for an hour it was filtered off with suction, washed with water and the copper salt decomposed with 500 ml. of a cold 25% solution of sulfuric acid. A small portion of the solid was not decomposed by this treatment and was filtered off and discarded. The acid solution was extracted twice with ether, first with 500 ml. and then with 300 ml. The ether solution was dried over calcium chloride, the ether distilled and the residue fractionated. The fraction between 130 and 142" was saved, dried over calcium

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[7] Morgan and Rawson, J. *Soc. Chem. Ind.*, 44,462 (1925).

[8] Morgan and Thomason, J. *Chem. Soc.*, 125, 754 (1924).

[9] Morgan and Holmes, *ibid.*, 125, 760 (1924).

[10] Morgan and Taylor, *ibid.*, 127, 797 (1925).

[11] Combes, *Ann. chim.* phys., [6]12, 250 (1887).

[12] Claisen and Lowman, *Ber.*, 21, 1151 (1888).

[13] Kutz: Acetylbenzoylisopropylmethane. Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.5; H, 8.0. Found: C, 76.4; H, 7.8.

[14] Trotman, J. *Chem. Soc.*, 127, 94 (1925).

chloride, decanted and then allowed to stand for two or three days with 3–4 g. of anhydrous potassium or sodium carbonate. The treatment with carbonate gave a final product which after distillation has remained colorless for over a year. After filtering off the carbonate the crude acetylacetone was fractionated. The fraction from 136–139° (uncorr.) was 120 g. or 60% of the theoretical based on the acetone introduced.

Acetylbenzoylmethane was obtained in the best yields by using two moles of sodium or one mole of sodium ethoxide per mole of acetophenone.[15] The procedure for the preparation was similar to that described for diacetylmethane up to the point where the reaction mixture was poured into water. At this point the sodium salt of acetylbenzoylmethane was filtered with suction, washed with benzene, dried in air, ground in a mortar and dissolved in water. The crude diketone was precipitated by acidification of the solution with acetic acid, filtered, dried and distilled under reduced pressure, 120–122° at 3 mm. or 128–130° at 10 mm. The yield was 208 g. or 64% based on the acetophenone. After recrystallization in an ethanol–water mixture the melting point was 56-67° (uncorr.).

Dibenzoylmethane was prepared as described in "Organic Syntheses"[16] and had a melting point of 76–78' (uncorr.).

Summary

The rate of alcoholysis at 60° of thirteen 1,3-diketones in the presence of hydrogen chloride has been studied. It has been shown that the rate of alcoholysis was independent of the ratio of diketone to alcohol when the latter was varied from 1:1 to 1:40. It was also independent of whether ethanol or butanol was used but fell off markedly with secondary propyl or tertiary butyl alcohol, due no doubt to the reaction of the latter with hydrogen chloride at 60° The alcoholysis of the diketones was not a reversible reaction in the presence of hydrogen chloride.

Acetylbenzoylmethane and benzylacetylbenzoylmethane which might split to give ethyl acetate or ethyl benzoate gave only the former ester.

The rate of alcoholysis and the apparent extent was a function of the amount of hydrogen chloride in the reaction mixture. A high ratio of catalyst to diketone (1:1) was necessary to secure practically complete alcoholysis of the most reactive of the diketones at 60° in forty-eight hours. The rate of alcoholysis of substituted diacetylmethanes fell off as the substituent was varied from n-butyl to n-propyl, ethyl, isopropyl, benzyl, diethyl and dibenzyl. Acetylbenzoylmethane underwent alcoholysis more slowly than did diacetylmethane. The introduction of a third substituent on the "methane carbon atom" still further inhibited alcoholysis.

Dibenzoylmethane underwent little or no alcoholysis under the conditions used for the alcoholysis of the other diketones investigated.

The maximum yields (60–65%) of diacetylmethane and acetylbenzoylmethane were obtained when the ratio of ketone to condensing agent was 1:1 for sodium ethoxide and 1:2 for sodium.

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[15] Cf. Claisen, *Ann.*, 291, 51 (1896).

[16] "Organic Syntheses," John Wiley and Sons, New York City, 1928, Vol. VIII, p. 60.

The preparation of isopropylacetylbenzoylmethane is reported for the first time.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

THE MECHANISM OF THE FORMATION OF HIGHER HYDROCARBONS FROM WATER GAS[1]

BY DAVID F. SMITH,[2] CHARLES O. HAWK[3] AND PAUL L. GOLDEN[4]

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Introduction

In April, 1926, Fischer and Tropsch[5] announced that higher homologs of methane are formed when mixtures of hydrogen and carbon monoxide are passed at atmospheric pressure over catalysts of iron or cobalt mixed with various supporting materials, at temperatures from 250 to 300°. The catalysts were stated to have been prepared by reduction from the oxides with hydrogen at 350°. It was said that no oxygen-containing organic compounds were found. The mechanism of the process was thought to be through formation of metallic carbides, although it was found impossible to obtain the higher paraffins by passing hydrogen alone over the supposed carbides. Upon further examination, Fischer and Tropsch[6] announced the product to consist of ethane, propane, butane and higher homologs up to solid paraffin, with only inappreciable amounts of olefins. It was said that a wide range of space velocities and $CO-H_2$ mixtures were used. Elvins and Nash[7] reported the formation of oily material on a cobalt–manganese oxide–copper catalyst at atmospheric pressure and temperatures from 245 to 284°. The yields were small, however. In July, 1926, Elvins and Nash[8] reported the presence of oxygen-containing compounds in addition to hydrocarbons in this product. Fischer and Tropsch[9] stated that oxygen-containing compounds were present in their product in only very small quantities compared to the amounts of hydrocarbons produced. At the September, 1927, Meeting of the American Chemical Society, Smith, Davis and Reynolds gave results of preliminary work in which olefin as well as paraffin hydrocarbons were obtained. Full details of this work

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[4] Assistant scientific aid, U. S. Bureau of Mines.

[5] Fischer and Tropsch, *Brennstoff-Chemie,* 7, 97 (1926); *Ber.,* 59, 830, *832* (1926).

[6] Fischer and Tropsch, *ibid.,* p. 923.

[7] Elvins and Nash, Fuel, 5, 263 (1926).

[8] Elvins and Nash, *Nature,* **118,** 154 (1926).

[9] Fischer and Tropsch, *Brennstoff-Chemie,* 7, 299 (1926).

were published later.[10] In December, 1927, Elvins[11] published the results of further work. The catalyst preparation received further attention and the products were examined more closely. Olefin and paraffin hydrocarbons were found as well as oxygen-containing compounds. Temperatures of 280–320° were used. In January, 1928, Fischer and Tropsch[12] gave the results of extensive examination of the gaseous and liquid hydrocarbons obtained. They report the presence of oxygen-containing compounds in small amounts and of only olefin and paraffin hydrocarbons. They stated that their products were obtained at reaction temperatures of around 190° on a cobalt–copper catalyst. Several hydrocarbons were identified. The presence of acetone and aldehydes in the water layer was claimed. Later, Smith, Hawk and Reynolds[13] presented complete results of the formation of olefin and paraffin hydrocarbons on a cobalt–manganese oxide–copper catalyst at temperatures of 200–260°. Good conversions were obtained, the lower hydrocarbons were completely analyzed, and complete information on the procedure was presented. The catalyst used here was much more active than the one used by Elvins and Nash. Since Fischer and Tropsch have not presented complete details of their work, it is not known just how active their catalysts were. Further examination of the hydrocarbon product by Tropsch and Koch[14] resulted in identification of various olefin and paraffin hydrocarbons. It showed the absence of naphthenes, but small quantities of benzene and toluene were found.

Nature of the Reactions

Elvins and Nash[8] suggest that the formation of oxygen-containing compounds is an intermediate step in the formation of hydrocarbons. Elvins[11] suggests that carbonyls are intermediate products. The latest presentation of the ideas of Fischer and Tropsch[12] on the possible mechanism of the process is outlined under (1), (2), (3) and (4) as follows. (1) Methylene (CH_2) may be formed primarily from hydrogen and carbide carbon, which is in turn at once polymerized to higher hydrocarbons. (2) Complex molecules of three and four carbon atoms may form as primary reaction products which also may in turn suffer polymerization. This possibility is discussed since propylene and butylene are the principal products when iron carbide is decomposed by acids, but the presence of ethylene and ethane in the synthetic product argues against this. (3) High molecular weight hydrocarbons may be formed in a primary act. These may undergo cracking on the catalyst. Thermodynamic relationships, Fischer and

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[10] Smith, Davis and Reynolds, *Ind. Eng. Chem.*, 20, 462 (1928).

[11] Elvins, *J. Soc. Chem. Ind.*, *46*, 473T (1927).

[12] Fischer and Tropsch, *Brennstoff-Chemie*, 9, 21 (1928).

[13] Smith, Hawk and Reynolds, *Ind. Eng. Chem.*, *20*, 1341 (1928).

[14] Tropsch and Koch, *Brennstoff-Chemie*, 10, 337 (1929).

Tropsch think, argue for this. (4) Secondary hydrogenation of olefins always occurs.

Passage of hydrogen alone over the supposed carbides produces no higher hydrocarbons, so that the "carbide theory" receives no support from this source. However, if the "carbides" are supposed to exist only transitorily and in the relatively small amounts which would be necessary to explain the catalysis, this theory becomes difficult to prove or disprove. In regard to possibility **(3)** above, obviously the fact that thermodynamically the formation of the very high hydrocarbons from water gas is possible, can have no bearing on the question of the mechanism. Before thermodynamic information was available it had been shown possible to derive these products from water gas under the experimental conditions of the process.

Evidently a reaction such as

$$20CO + 40H_2 = C_{20}H_{40} + 20H_2O$$

which is known to represent an over-all experimental result, can scarcely be imagined to take place in one step and at a rapid rate. In this sense, the reaction is a quite remarkable one. In an attempt to explain the mechanism of the reactions and to find means of better controlling them, the experimental work to be described herein was undertaken.

Experimental Work Using Cobalt–Copper–Manganese Oxide Catalysts

The general nature of the apparatus and method has been described elsewhere.[1] The possibility that cracking of the heavier hydrocarbons might occur on the catalyst during the process of their synthesis was first investigated. Using the cobalt–copper–manganese oxide catalyst previously described, a sample of our synthetic hydrocarbon oil (from which the products below pentane and amylene had been removed) was flushed over the catalyst at 206° with **137** liters of pure nitrogen in three hours. The original oil had a density of **0.7031,** an iodine number (Wijs) of **42.5** and weighed **20.83** g. The product collected after passage over the catalyst had a density of **0.7024,** an iodine number of **42.0** and weighed **19.56 g.** Only very small amounts of gaseous hydrocarbons were found in the nitrogen passing through. Thus no considerable amount of cracking (or polymerization) of these heavy hydrocarbons occurs and Fischer and Tropsch's suggestion, Number **3** above, seems to be excluded as far as forming any large part of the mechanism.

Next, it was desired to determine whether polymerization of the lower olefins occurred. Accordingly, pure ethylene was passed over the catalyst. No reaction whatever was observed. Similarly, a mixture of ethylene and hydrogen produced only ethane. Thus it seems that polymerization of ethylene is not a factor in the mechanism.

Mixtures of ethylene and carbon monoxide, when passed over the catalyst, gave no reaction. Likewise, ethylene and water vapor gave no reaction.

Since acetone was found by Fischer and Tropsch[12] to be a principal organic oxygen-containing compound, some experiments were undertaken to determine whether acetone might be an intermediate product in the formation of hydrocarbons. When a mixture of nitrogen and acetone vapor was passed over the catalyst at 206°, 4 to 7% of the acetone was converted to an oily product insoluble in water. Small amounts of hydrogen and methane appeared in the gas. The oil contained no acid or aldehyde. It was unsaturated. When a mixture of hydrogen and acetone was passed over the catalyst a considerable amount of hydrogen entered into reaction and considerably more methane was produced than was the case without hydrogen. A considerable amount of the product boiled in the range of ethyl alcohol, gave qualitative tests for primary and secondary alcohols, and contained no acid or aldehyde. About 0.1 cc. of heavy oil was produced. It melted from -2 to $+15°$ and was unsaturated. Some ethane appeared in the gas. Then, 55 g. of acetone was passed over the catalyst at 206° with 77 liters of water gas during the course of one and one-half hours. About 12 g. of the acetone entered into reaction. The product, aside from the usual hydrocarbons obtained from water gas alone, gave qualitative tests for primary, secondary and tertiary alcohols. Apparently, hydrocarbons may be produced from acetone. The hydrocarbons so formed, however, are different in character from those obtained from water gas. Although it is possible that some hydrocarbons arise through intermediate formation of acetone, the latter is practically never found in appreciable amount in the products and the results about to be described furnish a much better picture of the mechanism.

Although ethylene did not produce higher hydrocarbons either alone or in the presence of hydrogen or carbon monoxide, it was thought that in the presence of both hydrogen and carbon monoxide, this reaction might take place. Table I shows the results of the first experiments with ethylene–water gas mixtures. In the table it is to be noted that all gas volumes are reduced to standard conditions of temperature and pressure. In the data in this and following tables on products formed, g./l. H_2, etc., means grams of product obtained per liter of H_2, etc., converted in the process. The experiments were carried out in the order in which they are recorded in the table and with the same sample of catalyst (cobalt–copper–manganese oxide). They were all run at the same temperature and approximate rate for purposes of comparison. The straight water-gas experiments (the first and last in the table) were made in order to determine whether the activity of the catalyst was changing. Evidently the activity had remained substantially constant. The catalyst was flushed out with pure hydrogen overnight between experiments in order to assure that it remained free of

TABLE I

PRELIMINARY EXPERIMENTS WITH C_2H_4–CO–H_2 MIXTURES (250 CC. OF CATALYST)

Expt.	Temp., °C.	Flow rate liters/min.	Gas entering, liters H_2	CO	C_2H_4	N_2	Gas leaving, liters H_2	CO	C_2H_4	Gas converted, liters H_2	CO	C_2H_4
1	204	1.18	126	111	0	0	99	93	0.3	27	17	0
2	204	1.15	78	67	81	0	14	52	29	64	15	52
3	204	1.21	79	66	0	84	64	55	0.2	16	11	0
4	204	1.15	122	104	0	0	98	91	0.2	25	13	0

	Products formed								
Expt.	C_2H_6 liters	Pentane and higher g.	1 H_2	1 CO	1 H_2 + CO	CO_2 (g.)	H_2O (g.)	Sp. gr. of oil, 20°/20°	Iodine no. of oil
1	0.32	4.40	0.16	0.26	0.10	2.62	10.73	0.7120	73
2	40.5	12.69	.20	.86	.16	2.57	9.53	.7320	73
3	0.28	3.31	.21	.30	.12	1.98	7.87	.7219	79
4	..	4.38	.18	.34	.12	3.07	10.10	.7192	73

accumulated products and was completely reduced. Of course, oxidation of the catalyst by a trace of oxygen in the gas requires subsequent treatment with hydrogen at a higher temperature in order to reduce the catalyst completely. Analyses of the hydrocarbon products between ethane and pentane are not presented since they are not important for the present purposes. This fraction, however, was considerable in amount in an ethylene experiment as compared with that in a water-gas experiment. The yields are expressed in total liters or grams and in grams per liter of reactants converted in the process.

The original oil yield was separated from the water layer and carefully fractionated in a small apparatus to remove hydrocarbons lower than those of five carbon atoms.

In comparing Expts. 2 and 3, in which the partial pressures of carbon monoxide and hydrogen are the same but nitrogen has replaced ethylene, the striking thing is the large yield of oil in the presence of ethylene. Naturally, a large amount of ethylene is hydrogenated to ethane but about 11 liters of ethylene has been converted to oil. Due to the removal of hydrogen to form ethane, the yield of oil per liter of hydrogen converted is small, but the yield per liter of carbon monoxide converted is very large in Expt. 2. The larger consumption of carbon monoxide in Expt. 2 (reflected in the larger amounts of carbon monoxide and water appearing in the products) indicates that more of it enters into oil formation in the presence of ethylene. As was discovered later, the "oil" contains a considerable amount of oxygen-containing compounds. Recalling that ethylene does not react either alone or in the presence of either hydrogen or carbon monoxide, we find, however, when both carbon monoxide and hydrogen are present with ethylene, the latter enters into a reaction which produces heavier products. Thus, it seems that hydrogen and carbon monoxide react to produce substances on the catalyst surface with which ethylene is capable of reacting.

Upon examination of the product obtained from ethylene–water gas mixtures, it was found to contain 25 to 35% of water-soluble material (oxygen-containing compounds). This accounts for the higher density of the oil in Expt. 2. Of course, some of the water-soluble material was in solution with the water produced in the experiment, so that the total yield of organic products recorded in Expt. 2 should be increased by the amount which was removed with the water layer and the recorded amount of water should be decreased a corresponding amount. In an experiment at 210° in which the flow rate was 1.84 liters/minute and the ethylene concentration was 20 to 25%, the following results were obtained: original oil layer, 15.0 cc. (containing 30% of water-soluble material); original aqueous layer, 18.5 cc. Fractionation of this material gave: water, 14.0 cc.; hydrocarbon oil, 10.0 cc.; water-soluble organic material, 9.1 cc. Of course, due to possible existence of constant-boiling mixtures of water-soluble material with the water, the separation of the latter probably is not complete. In an ordinary experiment with water gas alone no appreciable amounts of water-soluble material were found in the oil, although a trace of aldehyde was usually present.

Comparison of Expts. **3** and 4 shows the effect of changing the partial pressures of carbon monoxide and hydrogen when the ratio $CO:H_2$ remains the same. At the lower partial pressures the amount of hydrogenation is less, as shown by the larger iodine number of the product in Expt. 3, and is reflected in the slightly increased yield of oil per liter of hydrogen converted. The presence of more unsaturated material in Expt. **3** is reflected in the higher density of the oil.

The results in Table II are presented in order to show the composition and amount of the intermediate hydrocarbon fraction in an ethylene experiment as compared with that in an experiment with water gas alone. Analysis of the intermediate hydrocarbon fraction was made using a modified Shepherd–Porter apparatus.[15]

TABLE II

COMPARATIVE EXPERIMENTS SHOWING COMPOSITION AND AMOUNT OF INTERMEDIATE HYDROCARBON FRACTION (250 CC. OF CATALYST)

Expt.	Temp., °C.	Flow rate, liters/min.	Gas entering (liters) H_2	Gas entering (liters) CO	Gas entering (liters) C_2H_4	Gas leaving (liters) H_2	Gas leaving (liters) CO	Gas leaving (liters) C_2H_4	Gas converted (liters) H_2	Gas converted (liters) CO	Gas converted (liters) C_2H_4
1	245	1.22	87	75	0	70	61	1.4	16	14	0
2	245	1.37	69	58	65	31	55	24	37	3	41

Expt.	Products formed, grams CH_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5H_{10} and higher	CO_2	H_2O	Sp. gr. of oil 20°/20°	Iodine number of oil
1	1.0	0.7	0.13	0.10	0.14	0.07	1.91	1.48	7.40	0.7041	116
2	2.0	45	0.88	0.22	1.15	0.17	3.70[a]	1.22	5.22[b]	0.7107	111

[a] This product contains 25% by volume of water-soluble material. [b] This product contains water-soluble organic material in large amount.

In order to show how the reaction of ethylene varied with its partial pressure and with the partial pressure of water gas present, the experiments recorded in Table III were performed. In comparing Expts. 1 and 2, it is noted that with lower partial pressure of water gas, the unsaturation of the product is increased and the total amount of reaction is less. The marked increase in oil yield when 22% of ethylene is added, keeping the partial pressure of water gas constant, is noted in comparing Expts. 2 and **3.** The yield of oil in Expt. 4 is still large, even when the ethylene concentration is reduced to 12%, keeping the water-gas concentration constant. In fact, the yield of oil seems not to change rapidly in this concentration range with change in the ethylene concentration. The percentage of

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[15] See Frey and Yant, *Ind.* Eng. *Chem.,* 19, 492 (1927).

water-soluble organic material in the oil of Expts. 3 and 4 was not determined accurately, although it definitely contained some—probably around 5%. In Expt. 5, when the water-gas concentration is increased keeping the ethylene at 22%, an increase is noted in the amount of reaction over that obtained in Expt. 3, as evidenced by increased yields of oil, carbon dioxide and water. The striking thing in the comparison of Expts. 3 and 5, however, is the large increase in amount of water-soluble organic material as the concentration of water gas is increased. It should be pointed out that the presence of ethylene in the water gas largely increases the yield of hydrocarbons excluding the water-soluble organic material. This is evident from the data in Table III.

TABLE III

DATA SHOWING THE DEPENDENCE OP THE REACTION OF ETHYLENE ON PARTIAL PRESSURE (250 CC. OF CATALYST)

Expt.	Temp., °C.	Flow rate, l./min.	Gas entering, liters H_2	CO	C_2H_4	N_2	Composition in % Water gas	C_2H_4	N_2	Gas leaving, liters Hz	CO	C_2H_4	Gas converted, liters Hz	CO	C_2H_4
1	211	1.10	118	103	0	0	100	0	0	108	94	0.2	10	9	0
2	210	1.24	53	44	0	149	39	0	61	46	38	0.2	7	6	0
3	213	1.31	53	41	54	95	38	22	40	16	37	21	37	4	33
4	213	1.27	56	40	31	122	39	12	50	21	34	5	35	6	26
5	206	1.29	82	58	49	34	62	22	15	41	49	14	41	9	35

Products formed

Expt.	CH_4, l.	C_2H_6, l.	Pentane and higher[b] g.	g /l Hz	g./l. CO	g./l. Hz + CO	CO_2, g.	H_2O, g.	Sp. gr. of oil, 20°/20°	Iodine number of oil	Water sol. comp in oil, %
1	2.9	0.3	2.83	0.29	0.30	0.15	3.40	7.66	0.7155	79	0
2	2 5	..	1.68	.25	0.28	.13	1.33	4.44	.7129	94	0
3	2 6	28	5.67	.15	1.42	.14	2.18	4.82"	.7188	131	<8
4	1.8	24	5.57	.16	0.90	.13	1.98	5 86[a]	.7183	121	<8
5	3.1	30	5.76	.14	0.68	.12	2.96	6.78"	.7500	130	30

[a] These figures include some water-soluble organic material. [b] In the ethylene experiments these figures include some water-soluble organic material.

The results in Table III suggested that oxygen-containing organic material originally formed was being converted to hydrocarbons on the catalyst. Accordingly, the experiments recorded in Table IV were made. In these experiments a measured amount of a sample of our oil containing both hydrocarbons and oxygen compounds was passed over the catalyst in a stream of gas. The products were collected in the usual manner. In order to vaporize the heavier material the sample was finally heated to the temperature of boiling water while the gas was passing through. The liquid product collected after passage over the catalyst in no case contained appreciable amounts of water-soluble material. It was far less unsaturated than the original material. Probably, elimination of water from the oxygen-containing compounds had occurred, accompanied by combination of the unsaturated residues. Possibly some of the decrease in unsaturation is due to hydrogen retained on the catalyst surface. The presence of carbon monoxide possibly prevents combination of the unsaturated residues of the dehydration, resulting in a more unsaturated product. This is further evidenced by the appearance of ethylene in the gas in this case. No carbon dioxide appeared in the products, so that the carbon dioxide which always appears during the synthesis of hydrocarbons from water gas probably arises either in a way different from that in which the water does, or the elimination of carbon dioxide from intermediate products is so rapid that this type of intermediate compound does not persist.

TABLE IV

BEHAVIOR OF THE OXYGEN-CONTAINING COMPOUNDS WHEN CARRIED OVER THE CATALYST IN A GAS STREAM (250 CC. OF CATALYST)

Expt.	Temp., °C.	Gas used as carrier	Oil in Cc.	Oil in W. S., %	Oil in I_2 no.
1	211	N_2	5.0	40	130
2	211	H_2	4.5	40	130
3	211	CO	4.5	40	130

Expt.	Gas leaving, liters CO	H_2	N_2	CH_4	C_2H_4	C_2H_6	Oil out Cc.	Oil out I_2 no.	H_2O formed, cc.
1	0.05	0.6	47.5	0.4	0	0.2	3.1	6	0.5
2	0.05	51.3	0	1.4	0	.18	2.2	6	.6
3	51.9	1.2	0	0.5	0.03	0	2.8	90	.7

It may be of interest to consider the effect on the reaction of varying ratios of H_2:CO. This is shown in Table V. Experiment 1 shows the use of ordinary water gas. As shown in Expt. 2, at approximately the same temperature an increase of hydrogen concentration causes a largely increased reaction which, however, results principally in methane formation. With approximately this same mixture, when the temperature is lowered as in Expt. 3, the methane formation is reduced but the oil yield is still only three-fourths of normal. When the hydrogen concentration is lowered with corresponding increase in the carbon monoxide concentration, very little reaction of any kind takes place. The oil in Expt. 2 is nearly saturated. However, in Expt. 4 a large decrease in the hydrogen concentration over that prevailing in Expt. 3 does not produce a corresponding unsaturation in the oil. The latter effect is doubtless to be attributed to the fact that the relatively large total consumption of hydrogen in Expt. 3 reduces the hydrogen concentration at the point where reaction is occurring. In Expt. 2, the slower rate as well as the high hydrogen concentration favors saturation of the product. The water layer from Expt. 4 was found to contain a small amount (about 0.5%) of acetone. This is the only case where the presence of acetone was definitely established in an experiment with a gas containing only carbon monoxide and hydrogen on a cobalt catalyst.

TABLE V

EFFECT ON THE REACTION OF VARYING RATIOS OF H_2:CO (250 Cc. OF CATALYST)

		Flow	Entering gas, liters		Composition of entering gas, %		Gas leaving, liters		Gas converted, liters	
Expt.	Temp., °C.	rate, l./min.	H_2	CO	H_2	CO	H_2	CO	H_2	CO
1	225	1 28	123	107	54	42	108	94	15	14
2	220	1.06	115	28	77	19	52	0.7	63	28
3	207	1.25	185	53	75	22	170	42	15	11
4	207	1.13	50	172	22	77	47	164	3	8

	Products formed										
				Pentane and higher						Sp. gr.	Iodine
Expt.	CH4, g.	C_2H_4 g.	C_2H_6, g.	g.	g./l. H_2	1 CO	g./l. Hz + CO	CO_2, g.	H_2O, g.	of oil, 20°/20°	number of oil
1	...	...	..	3.94	0.26	0.29	0.14	262	902	07182	88
2	16.7	0.02	1.14	0 98	.16	.036	.011	10.21	18.6	.7098	4
3	3 8	.52	0.12	3.00	.20	.29	.12	1.18	7.87	.7090	64
4	1.0	.15	..	0 7	.2	.1	.07	1.15	3.00	...	79

Experimental Results Using Cobalt–Copper Catalyst.—Cobalt–copper catalysts were prepared by the same general method that was used in preparing the cobalt–copper–manganese oxide catalyst. They showed no striking differences in behavior except that they were somewhat less active. It is thought, however, that their activity could be increased by improvements in the method of preparation. In general, a somewhat lighter oil and more carbon dioxide relative to water were produced.

Experimental Results Using Iron–Copper Catalyst.—From the practical standpoint we have found the iron–copper catalysts to be the most satisfactory we have used. When properly prepared they are very hard and strong, relatively insensitive to overheating and produce little or no methane in spite of the fact that the temperature required is 30–40° higher than is necessary for the same conversion with cobalt–copper–manganese oxide catalysts.

Catalyst Preparation.—A hot solution of ferric and copper nitrates, in which the atomic ratio Fe : Cu was 4:1, was precipitated by slowly stirring in a solution of sodium hydroxide. The precipitate was thoroughly washed by decantation until it began to become colloidal. It was then dried very slowly until it started to form a gel which was of suitable consistency for molding by forcing through a grease gun. The molded material was then dried slowly up to a final temperature of 200", at which point it shows a metallic luster and fracture. It was then very slowly reduced in place by a mixture of hydrogen and nitrogen at 150°, gradually increasing the partial pressure of hydrogen and the temperature until finally pure hydrogen was used at 285°. The reduced material is pyrophoric and its hardness is decreased by the rapid oxidation which takes place upon exposure to air. It is necessary to avoid the presence of chlorides since they are very difficult to wash out of ferric hydroxide precipitates and if allowed to remain, according to our experience, reduce the activity of the resulting catalyst. Probably some small amount of alkali is retained in the catalyst. The effect of this is not definitely known.

Results obtained with the iron–copper catalyst are shown in Table VI. The extremely small amount of methane produced is to be noted as well as the small amounts of the intermediate hydrocarbon fraction and, in contrast to results with cobalt catalysts, the great preponderance of carbon dioxide over water.

TABLE VI

RESULTS OBTAINED WITH TWO PREPARATIONS OF IRON–COPPER CATALYST[a] (200 CC. OF CATALYST)

Expt.	Temp., °C.	Flow rate, l./min.	Gas entering, liters H_2	Gas entering, liters CO	Gas leaving, liters H_2	Gas leaving, liters CO	Gas converted, liters H_2	Gas converted, liters CO
1	256	1.23	142	125	124	93	18	32
2	266	1.16	129	94	104	50	25	44

Products formed

Expt.	Methane[b] g.	Methane[b] g./l. H_2	Methane[b] g./l. CO	Methane[b] g./l. H_2 + CO	Ethylene g.	Ethylene g./l. H_2	Ethylene g./l. CO	Ethylene g./l. H_2 + CO
1	0.82	0.045	0.026	0.016	1.26	0.068	0.039	0.025
2	Too small to detect				1.39	.057	.031	.020

Products formed

Expt.	Ethane g.	Ethane g./l. H_2	Ethane g./l. CO	Ethane g./l. H_2 + CO	Pentane and higher g.	Pentane and higher g./l. H_2	Pentane and higher g./l. CO	Pentane and higher g./l. H_2 + CO
1	1.49	0.081	0.046	0.030	5.78	0.31	0.18	0.11
2	1.36	.055	.031	.020	8.37	.34	.19	.12

Products formed

Expt.	CO_2 (g.)	H_2O (g.)	Sp. gr. of oil 20°/20°	Iodine number of oil
1	35.6	3.1	0.7294	106
2	48.0	2.7	.7340	119

[a] The amount of the intermediate hydrocarbon fraction was too small to analyze accurately. [b] The results for methane are not very accurate on account of the small amounts obtained and on account of the presence of small amounts of methane in the water gas used.

In experiments in which the water gas contained ethylene, it was found that the ethylene did not enter into reaction at all and that no oxygen-containing compounds were obtained. This indicates that if intermediate, oxygen-containing compounds are formed, they are quickly decomposed to produce hydrocarbons, as was suggested for compounds which tend to eliminate carbon dioxide, in connection with the results on cobalt catalysts. However, it seems here that the mechanism of hydrocarbon formation differs essentially from that obtaining on cobalt catalysts in that ethylene does not increase the yield of oil. The small quantities of methane formed here, considered with respect to the considerably larger amounts formed on the cobalt catalyst and the methane formed when the oxygen-containing compounds decompose on the cobalt catalysts, suggest that the methane formation always noted with the cobalt catalyst arises during the dehydration of these oxygen-containing compounds. Some of the differences in behavior of cobalt and iron catalysts may be due, of course, to the difference in temperature—particularly some of the difference in the ratio CO_2:H_2O, since this has been shown to increase with increased temperature on the cobalt catalyst.

With the iron–copper catalysts used here, the oil formed was heavier than that obtained with cobalt catalysts. It contained about 3% of very heavy hydrocarbons insoluble in acetone. The product from the cobalt catalysts contained none of these.

Experiments Using Iron–Copper–Manganese Oxide Catalysts.—Catalysts consisting of iron, copper and manganese oxide were prepared by the same general method used for the iron-copper catalysts. The activity of the catalyst, its physical properties and its action were quite similar to those of the iron–copper catalyst. One point of interest was a test made on its susceptibility to poisoning. Short tests failed to show any poisoning action when using water gas from which hydrogen sulfide had been removed but which retained its original content of organic sulfur.

Mature of the Oxygen-Containing Compounds Formed on Cobalt Catalysts When Using Water Gas Containing Ethylene.—Only recently have we obtained larger quantities of the oxygen-containing compounds formed from water gas–ethylene mixtures on cobalt catalysts. A careful examination of this product should be made. As yet we have only the following qualitative observations: aldehydes and alcohols are present; methyl alcohol, acids, esters and acetone are not present; the whole product boils below 100°. Boiling points of the pure constituents cannot be deduced from this latter fact since constant boiling mixtures are doubtless formed.

Discussion of Results

The work presented in this paper shows that cracking of the heavier hydrocarbons does not play any considerable part in the formation of the mixture of hydrocarbons higher than methane, when the synthesis is carried out on a cobalt–copper–manganese oxide catalyst under the conditions described. The experiments in which acetone was passed over the catalyst with hydrogen, nitrogen or carbon monoxide indicate that acetone likewise is not a predominating intermediate. Acetone is almost never present in the products from water gas alone. Polymerization of ethylene or of higher olefins does not occur.

Ethylene, at least in concentrations over 10%, enters into reaction upon the cobalt–copper–manganese oxide catalyst in the presence of water gas, forming higher hydrocarbons and large quantities of oxygen-containing compounds. The oxygen-containing compounds dehydrate to a greater or less extent, producing hydrocarbons. The dehydration is accompanied by some polymerization. The extent to which ethylene enters into these reactions does not change largely with the ethylene concentration when this is above about 10%, but the formation of these intermediate products depends quite markedly upon the concentration of water gas. These facts make it seem likely that these oxygen-containing compounds form the intermediate products in the synthesis of hydrocarbons under these conditions from water gas which does not contain added ethylene. Similar experiments with still lower concentrations of ethylene would be desirable. We have not yet determined whether the higher olefins act similarly to ethylene, but presumably they do, to some extent at least. The mechanism by which the hydrocarbons are formed may be regarded as follows. There is some association of hydrogen and carbon monoxide on the catalyst surface. This complex may either decompose, giving an olefin and water, or ethylene or other olefin may combine with it to form an oxygen-containing compound which may either pass into the products or eliminate water to form a higher olefin hydrocarbon. The olefins are to be regarded as the primary hydrocarbon products. They may later be hydrogenated to form paraffin hydrocarbons or pass on into the products, depending upon the experimental conditions of hydrogen concentration, space velocity, catalyst and temperature.

The mechanism of the reactions on the iron catalyst is essentially different from that on the cobalt catalyst, aside from the fact that carbon dioxide is predominant instead of water, since ethylene does not enter into the reaction in this case. The extremely small amounts of methane ordinarily formed on iron–copper catalysts in contrast to the appreciable amounts from the cobalt catalyst (which may quite likely arise during dehydration of the intermediate oxygen compounds in this case) also suggest a different mechanism. It is possible that further experiments with iron–copper catalysts at lower temperatures or higher space velocities may permit isolation of some intermediate product.

Summary

1. It has been shown that in mixture with carbon monoxide and hydrogen, ethylene reacts on a cobalt–copper–manganese oxide catalyst to form large quantities of higher hydrocarbons and oxygen-containing compounds. The latter may dehydrate to form hydrocarbons. The dehydration may be accompanied by polymerization. Alone, or with either carbon monoxide or hydrogen, ethylene does not form higher hydrocarbons under the conditions described. The cracking of heavy hydrocarbons does not form a considerable part of the process. Acetone is not an important intermediate product. The higher olefins do not polymerize under these experimental conditions.

2. The mechanism of hydrocarbon formation on an iron–copper catalyst is essentially different from that on a cobalt–copper–manganese oxide catalyst, aside from the relative amounts of carbon dioxide and water formed, since in this case ethylene docs not enter into reaction.

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APPLICABILITY OF THE QUINHYDRONE ELECTRODE TO UNSATURATED ACIDS

BY W. H. HATCHER AND M. G. STURROCK

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In the course of studies of the reaction of hydrogen peroxide on organic substances, it was found necessary to prepare dihydroxymaleic acid, and the method used was that of Fenton,[1] more recently detailed by Nef.[2] The technique of this method after many trials was found to be so unsatisfactory, and experiments performed on the purified product showed such conclusive evidence of further reaction with hydrogen peroxide, that it was decided to study the mechanism of the Fenton Reaction in this particular.

Briefly stated, this reaction results from treating tartaric acid with dilute hydrogen peroxide in the presence of ferrous sulfate, the dihydroxymaleic acid being precipitated by fuming sulfuric acid later. It was found possible to increase the very small yields characteristic of this reaction; but, after many experiments involving every possible variation of conditions governing the reaction, definite data were obtained to show that it was the hydrogen-ion concentration of the mixture which prevented more than one-third of the theoretical quantity of hydrogen peroxide from reacting to form dihydroxymaleic acid. It was planned to decompose the excess peroxide by means of platinum black and to employ the very convenient quinhydrone electrode to determine the hydrogen concentration of the mixtures of dihydroxymaleic and tartaric acids produced during the course of the reaction. That this method was unsuitable is shown in the following data. It should be added, however, that further experiments now nearing completion justify the previous ideas as to the very important part played in this reaction by hydrogen ions.

Biilmann and Lund[3] were responsible for the development of the quinhydrone electrode method for PH determination in acid solution, and they recommended its use because of the simplicity of its technique and because of its superior applicability over the hydrogen electrode to unsaturated compounds. It is shown below that the quinhydrone electrode is not applicable when the tendency of the solution to reduce is such that the ratio of hydroquinone to quinone is seriously altered.

Very often, however, advantage may be taken of the slowness with which some such oxidation–reduction potentials attain equilibrium. Such acids as maleic and fumaric fall into the class of substances whose PH may be thus determined. When the equilibrium is instantaneously or rapidly

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[1] Fenton, *J. Chem. Soc.*, **75**, 575 (1899).

[2] Nef, *Ann.*, 257, 290 (1907).

[3] Biilmann and Lund, *Ann. chim.*, [9] 15, 109 (1921); [9] 16, 321 (1921).

attained, the method is useless. Such unusual ease of reduction has been found in the case of dihydroxymaleic acid.

Experimental

Preliminary experiments using dihydroxymaleic acid and the usual amount of quinhydrone (approx. 0.01–0.02 g.) showed that no constant value could be immediately obtained. The readings were at first low, increasing to a maximum and then falling off to a constant level. Addition of further quinhydrone caused a repetition but a slightly higher final level was attained, and so on until addition of still more quinhydrone caused no further change.

TABLE I

DIHYDROXYMALEIC ACID, 0.00825 M

Quinhydrone added in five portions of 0.02 g. each (0.02 g. of quinhydrone was found sufficient to take a second solution of 0.06585 M maleic acid to a constant reading of 319.5 millivolts in 3045 sec.)

Time	No. 1	No. 2	No. 3	No. 4	No. 5
15 Sec.	163	180	233	260	266
30 Sec.	145	168	243	264	267
45 Sec.	. . .	152	245	264	270
60 Sec.	132	152	251	264	270
1.5 Min.	132	152	251	265	270
2.5 Min.	[a]	[b]	[c]		
15 Min.	132	152	251	265	270.5

[a] Quinhydrone gone in 45 sec. Soln. then colorless. [b] Soln. colorless in 60 sec. [c] Faint yellow color remaining at end of 2 min.

Confirmation of Assumption that the Dihydroxymaleic Acid is Reduced to Tartaric Acid by the Hydroquinone.—0.0376 g. of dihydroxymaleic acid on reduction would give 0.0376 × (150/184) = 0.03065 g. of tartaric acid.

TABLE II

TARTARIC ACID. CONCN. 0.03065 G. IN 24.84 CC.

Time, sec.	No. 1	No. 2	Time, min.	No. 1	No. 2
15	260	263	1.5	270	271
30	265	267	2.5	270.5	271
45	268	270	5	270.5	271
60	268.5	271	15	270.5	271

Discussion of Results

The results with dihydroxymaleic acid show that the quinhydrone electrode cannot be used in the case of this unsaturated acid; 0.02 g. of quinhydrone is sufficient to produce a uniform and constant pressure of hydrogen under ordinary conditions. No constant readings could be obtained using this acid until more than three or four times the above amount of quinhydrone had been added. The obvious conclusion is that there has been reaction between the quinhydrone and dihydroxymaleic acid. Since hydroquinone is a reducing agent and dihydroxymaleic acid possesses a double bond, it is quite reasonable to suppose that the acid is reduced to tartaric. That such is the case is shown in the last table, in which tartaric acid was used in such a concentration as would result when **0.0376** g. of dihydroxymaleic acid is reduced at the ethylene linkage.

Moreover, assuming that each gram molecule of quinhydrone contributes **2** g. of hydrogen, **0.08** g. would provide **0.00073347** g. of hydrogen; **0.0376** g. of dihydroxymaleic acid requires **0.0004087** g. of hydrogen and constant readings should be obtained using this amount; **0.06** g. would supply **0.0004396** g. of hydrogen for the reduction of the acid and the remaining **0.02** g. produces the pressure of hydrogen ions at the electrode.

Pirie and Pinhey[4] have observed that glutathione, a substance well known to be very easily oxidized and reduced, has a similar effect in upsetting the quinone–hydroquinone equilibrium. Dihydroxymaleic acid, therefore, may be compared to glutathione with respect to the ease with which it may be reduced.

Conclusion

It is shown above that the quinhydrone electrode is not applicable to all unsaturated acids.

From the standpoint of a study of this acid, the results are doubly interesting since they indicate the reactivity of this double bond, heavily laden as it is with highly negative groups.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

PREPARATION OF SOME CYCLOPENTANE DERIVATIVES

BY W. R. EDWARDS, JR.,[1] AND E. EMMET REID

RECEIVED MARCH 18, 1930 PUBLISHED AUGUST 5, 1930

Alicyclic compounds are known to be present in many crude petroleums as well as in a variety of other natural substances. When their diversity and the number of their theoretically possible modifications are considered, our knowledge of them seems relatively meager. In the present work a study has been made of the reactions between cyclopentylmagnesium halides and a variety of aldehydes. Previous employment of the former in the Grignard reaction has been confined to a very few instances, cyclopentylsulfonic acid,[2] cyclopentylcarboxylic acid,[3] cyclopentyl carbinol[3,4] and γ-cyclopentylpropanol[5] having been made thereby.

[4] Pirie and Pinhey, J. *Biol.* Chem., 74, 323 (1929).

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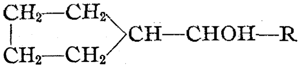
[1] From the Ph D. dissertation of W. R. Edwards, Jr., 1928.

[2] Borsche and Lange, Ber., 40, 2220 (1907).

[3] Zelinsky, *ibid.*, 41, 2627 (1908).

[4] Wood and Scarf, J. *Soc.* Chem. *Ind.*, 42, 13T (1923).

[5] Adams and Noller, THIS JOURNAL, 48, 1080 (1926).

We have obtained and characterized a new series of secondary alcohols of the type  where "R" represents the following radicals: methyl, ethyl, *n*-propyl, *n*-butyl, n-hexyl and phenyl. An attempt to obtain the anisyl derivative was unsuccessful owing to the pronounced decomposition of the product on distillation. For characterization, crystalline derivatives of these carbinols have been prepared.

As the starting point for these syntheses, cyclopentanone was made from commercial cyclohexanol by standard methods and reduced both by standard methods and by the method of Wislicenus and Hentzschel[6] and by the catalytic method of Adams and his co-workers,' to cyclopentanol. Certain modifications tending toward better yields or greater convenience and rapidity were introduced into these processes. Both the bromide and the chloride were prepared from cyclopentanol and employed in the earlier part of the work; but as the bromide proved more satisfactory, it was used exclusively for the later preparations. The magnesium complex usually formed readily and reacted smoothly with the aldehydes. The resulting carbinols are high-boiling liquids, and received their final purification by fractionation at reduced pressures. The alkyl derivatives showed no signs of decomposition during distillation; but the phenyl derivative was slightly affected, and the anisyl product was very largely decomposed.

Table I gives a number of the constants of these compounds. The five alkyl cyclopentyl carbinols exhibit fairly regular elevation in boiling point and decrease in density as the number of carbon atoms increases. Since

TABLE I

DATA ON COMPOUNDS

Compound C_5H_9CHOHR R =	Boiling points				Densities		Refr. index	Mol. refr. $[(n-1)M]/d$	Melting points, °C. (corr.)			Analysis			
	Press., mm.	Temp., °C. (corr.)	Press., mm.	Temp., °C. (corr.)	25°/4°	0°/4°			3,5-dinitro benzoate	Phenyl- urethan	α-Naphthyl urethan	Found C	Found H	Calcd. C	Calcd. H
Methyl	31–32	73.5–75	52.5	85–85.5	0.9163	0.9342	1.45 1	56.55	86	71–71.5°	104	73.46	12.29	73.61	12.37
Ethyl	18	72 574.5	52.5	97.5–98.5	.9035	.9219	1.4502	6384	83.5	Oil	91	74.77	12.48	74.92	12.59
n-Propyl	..	...	52	114.5–115.5	.8970	.9146	1.4510	71.46	85	Oil	85	75.79	12.75	75.98	12.76
n-Butyl	23	114–115			.8935	.9115	1.4548	79.48	63.5	Oil	..	76.51	12.80	76.85	12.91
n-Hexyl	12–12.5	129.5130.5			.8848	.9012	1.4562	94 97	Oil	Oil	Oil	77.88	12.96	78.19	13.13
Phenyl	5	129–131			1.0346	1.0531	....	...	Oil	Oil	..	80.96	8.51	81.76	9.16

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[6] Wislicenus and Hentzschel, *Ann* , 275, 322 (1893).

[7] Adams and Noller, Ref 5, and earlier work by Adams and co-workers.

this work was done Bedos[8] has prepared the methylcyclopentyl carbinol in an entirely different way. He gives the melting point of the phenylurethan as 70–71°.

In general, the by-products of the Grignard reactions were not examined; but one unexpected secondary reaction was noted and studied. During the reaction between benzaldehyde and cyclopentylmagnesium bromide, a small quantity of a substance identified as 1,3-dibenzylidene-cyclopentanone-2 was formed. It was first observed after the Grignard complex had been decomposed with dilute hydrochloric acid; after standing overnight, yellow needles of the compound, which is only slightly soluble in cold ether, were observed. The attempt to prepare anisylcyclopentyl carbinol was made in order to determine whether or not a similar secondary reaction would take place. Crystals appeared in the same manner, and were identified as 1,3-di-*p*-methoxybenzylidene-cyclopentanone-2, the condensation product of anisic aldehyde with cyclopentanone.

Compounds of this type are readily formed[9] by condensation of one molecule of cyclopentanone with two molecules of an aromatic aldehyde, under the influence of certain condensing agents, of which hydrochloric acid is one. One of the possible explanations of this occurrence is that the cyclopentyl bromide employed in the reaction retained a small amount of cyclopentanone, that this cyclopentanone in some manner resisted the normal tendency to unite with the cyclopentylmagnesium bromide as soon as the latter was formed, and that it did react with a portion of the benzaldehyde, under the influence of the hydrochloric acid, following the addition of the latter. Steric hindrance might account for its failure to form completely a complex with cyclopentylmagnesium bromide, or for its displacement from such a complex by benzaldehyde. It is of interest to note that Sabatier and Mailhe[10] working with the analogous cyclohexyl compounds, succeeded in forming 1,1-cyclohexylcyclohexanol from cyclohexylmagnesium chloride and cyclohexanone; but that they report that there is much secondary action, and that the yield "is not very good." The quantity of cyclopentanone which would have had to be present to account for the quantity of crystals formed would be equivalent to a little more than 1% of the quantity of cyclopentyl bromide. The latter was actually found to contain a trace of the ketone.

To test this theory, a further experiment was made, using the cheaper cyclohexyl compounds, in the belief that they would behave sufficiently like their cyclopentyl prototypes. Cyclohexyl chloride was prepared and divided into two portions, A and B. A small portion of cyclohexanone was added to **A**, while B was subjected to a careful treatment designed to

[8] Bedos, Compt. rend., 189, 255 (1929).

[9] Vörlander *and* Hobohm, *Ber.*, 29, 1840 (1896).

[10] *Sabatier and* Mailhe, *Ann. chim. phys.*, [8] **10**, 547 (1907).

remove any trace of ketone. Each portion was then used to form cyclohexylmagnesium chloride, which was treated in the usual manner with benzaldehyde, followed by hydrochloric acid. From the reaction employing portion A, a fair quantity of 1,3-dibenzylidene-cyclohexanone-2 was obtained; but no trace of this compound could be found in the products of the reaction employing portion B. The result of this experiment strengthens the above explanation.

A further experiment, in which cyclohexyl chloride containing cyclohexanone was used, and a very slight excess of dilute acetic acid substituted for hydrochloric acid as the neutralizing agent, failed to yield any of the condensation product, establishing the hydrochloric acid as the condensing agent.

Experimental

Preparation of Adipic Acid.—This was prepared from commercial cyclohexanol, by oxidation with boiling concentrated nitric acid, employing the method described in "Organic Syntheses."[11] Stirring proved unnecessary, since active boiling with a sufficient excess of the acid ensured rapid and complete conversion. By using a five-liter balloon flask containing 2 liters of nitric acid, it was possible to convert 625 g. of cyclohexanol in a single run. After washing with 100 cc, of cold 1:3 nitric acid, followed by 150 cc. of ice water, and air-drying on a porous plate, the adipic acid crystals were nearly white, and suitable for further use; yield, 55%.

Preparation of **Cyclopentanone.**—The method described in "Organic Syntheses"[11] was followed.

Preparation of **Cyclopentanol.**—(1) With sodium and moist ether, by the method of **Wislicenus** and **Hentzschel.**[6] This reaction was hastened by siphoning off the water layer occasionally as the concentration of sodium hydroxide increased, and adding fresh water. The yields never exceeded 30% and often ran lower. No cyclopentanone was recovered, the loss apparently being due chiefly to pinacone formation. Although several reduction units were maintained in simultaneous operation, the method was still very slow and required constant attention. It was therefore abandoned in favor of the catalytic method.

(2) With hydrogen and platinum-oxide platinum black catalyst, by the method of Adams and his co-workers. The procedure was essentially that described briefly by Adams and **Noller**[5] and more fully by Adams and **Yohe,**[12] using the apparatus described by Adkins and **McElvain,**[13] except that a 20-liter tank was used as the low-pressure hydrogen reservoir, and a quart ginger-ale bottle as reaction vessel, the latter being mounted in a cradle so designed as to reinforce it on all sides. From one to one and a half moles could be converted in this at a single run. The platinum oxide was prepared by the method of Adams and **Voorhees.**[14] From 1.5 to 2.5 g. of platinum oxide was placed in the reduction vessel, and 250 cc. of ethyl alcohol (95%) was added. Hydrogen at 3–4 atmospheres was applied, with shaking, for ten minutes, to reduce the oxide. Eighty-four grams (one mole) of freshly distilled cyclopentanone was then

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[11] "Organic Syntheses," John Wiley Sons, Inc., New York, Vol. V, 1925, p. 9.

[12] Adams and **Yohe,** THIS JOURNAL, 50, 1503 (1928).

[13] **Adkins** and **McElvain,** "Practice of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1925, p. 277.

[14] Adams and Voorhees, THIS JOURNAL, 44, 1402 (1922). See also Adams and Shriner, *ibid.*, 45,2171 (1923).

added, hydrogen re-applied, and shaking continued until the drop in pressure indicated the required amount of absorption. The catalyst was then filtered off and the solution fractionated through an 86-cm. (34-inch) column; yield, 85–90%.[15]

Preparation of Cyclic Chlorides and Bromides.—Cyclopentyl and cyclohexyl chlorides were made by refluxing the corresponding alcohols with excess of concentrated hydrochloric acid. The former required three hours and the latter eighteen hours of refluxing for best results. A considerable quantity of cyclopentene was formed during the preparation of cyclopentyl chloride. The chlorides were washed with dilute sodium carbonate, dried aad fractionated. Cyclopentyl bromide was prepared from cyclopentanol and phosphorus tribromide by the method of Adams and Noller.[5]

Freparation of Phosphorus Tribromide.—The method used was suggested but not described by Turner and Bury.[16] In a one-liter balloon flask fitted with a reflux condenser and a dropping funnel were placed 150 g. of carbon tetrachloride and 48 g. of finely divided red phosphorus. With cooling and frequent shaking, 360 g. of bromine was added drop by drop, after which the mixture was refluxed gently for fifteen minutes. It was then filtered and the filtrate distilled. The portion boiling between 170 and 175° was redistilled just before using, and the 173–175° fraction was employed in making cyclopentyl bromide. The yield, about 50%, was considerably less than that obtained in the usual way, by employing benzene and white phosphorus but it was obtained and purified with greater ease.

Freparation of Methyl Cyclopentyl Carbinol.—In a one-liter balloon flask, fitted with a dropping funnel, 70-cm. condenser, and motor-driven mercury-sealed stirrer, were placed 150 cc. of dry ether and 18 g. of magnesium turnings, and 77 g. (0.73 mole) of cyclopentyl chloride, in 120 cc. of ether, was added drop by drop. The reaction required cooling for a few minutes, and then continued to generate sufficient heat to maintain ebullition for nearly an hour. The solution was refluxed on a water-bath for an hour, allowed to stand for two hours surrounded with an ice-water-bath, and treated slowly with 33 g. of acetaldehyde in 120 cc. of ether. The mixture was allowed to stand overnight, refluxed for fifteen minutes and treated with crushed ice, followed by a slight excess of dilute hydrochloric acid. The ethereal portion was separated and combined with several ethereal extracts of the water laver. It was then washed with potassium carbonate solution, the wash liquid being subsequently extracted with ether, which was added to the main portion. After drying over two successive portions of potassium carbonate, the ether was distilled on a water-bath. The residue was placed in a flask

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[15] Information supplied by G. R. Yohe (private communication) and since published[11] was very helpful in carrying out this reduction. We noticed a number of peculiarities in the process, some of which merely corroborate Adams and Yohe's observations, and others which appear to be new. Reduction was decidedly more rapid in ethanol than in methanol. Addition of the ketone before reduction of the catalyst or repeated use of the same catalyst without re-solution and reprecipitation, caused a very marked diminution in yield, apparently greater than that experienced by Adams and Yohe. After a pronouncedly unsuccessful run, the use of anything involved in that run, catalyst, ketone, solvent or vessel, without rigorous purification, would usually spoil subsequent attempts. These observations seem to indicate that the catalyst was constantly undergoing slow poisoning from some undetermined source.

It was also noted that there was a rather sharp dividing line between the speed of shaking which gave maximum rate of conversion, and a speed which gave a much inferior rate. For best results, it was necessary for shaking to be sufficiently violent to throw the platinum particles to the surface of the solution, and to the walls of the vessel above the surface.

[16] Turner and Bury, *J. Chem. Soc.*, **123**, 2489 (1923).

with a 38-cm. (15-inch) fractionating column, and subjected to fractionation at reduced pressure. The principal cut was redistilled twice, ultimately yielding 11 g. of a colorless liquid, boiling at 85–85.5° at 52.5 mm. It had a pleasant penetrating odor, resembling that of menthol. Its constants are listed in the accompanying table. While the quantity obtained corresponds to a yield of only 13%, it is probable, taking into account losses through evaporation and comparing the quantities obtained in each successive fractionation, that the total amount of the carbinol formed in the reaction was about 40%.

Preparation of Ethyl, n-Fropyl, *n*-**Butyl** and n-Hexyl Cyclopentyl **Carbinols.**—These were prepared as was the methyl compound, 1 mole of cyclopentyl bromide being used in each case except for the propyl, where it was only 0.3 mole. The addition of the amyl and heptyl aldehydes to the Grignard reagent gave comparatively little heat and the resulting complexes were soluble in ether. The yields were 19.5, 12, 18 and 11%, respectively, of the twice distilled products. The odors resembled that of the methyl compound except that the propyl suggested olives and the hexyl resembled n-heptanol.

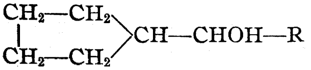
Freparation of Phenyl Cyclopentyl **Carbinol.**—The reaction proceeded in the usual manner, except for the appearance of the crystals previously described, which were removed before distillation. A dark tarry residue remained when the ether was distilled and the higher-boiling liquid decanted. The latter was distilled from a Claisen flask at 5 mm. A fraction boiling between 129 and 131°, chiefly at 130°, was obtained, its distillation being accompanied by the appearance of a certain amount of decomposition. Freshly distilled, it possessed a light brown color, which changed, during a period of several weeks, to a very dark brown. A large quantity of tarry residue remained in the flask, and a little unchanged benzaldehyde was recovered. The yield of rather impure carbinol was about 7%.

Attempt to Prepare Anisyl Cyclapentyl **Carbinol.**—The usual addition of the aldehyde produced only a small amount of heat. After removal of the condensation product previously described, the ether was distilled and the remaining liquid decanted and fractionated from a Claisen flask at 5–6 mm., to the accompaniment of much apparent decomposition. A rapidly-darkening, fairly constant-boiling cut of 12 g. was obtained in the neighborhood of 156" at 5–6 mm. On redistillation, decomposition was even more marked and the boiling point was not more definite. Analysis of the final product showed: C, 68.82; H, 8.07 (theoretical for anisyl cyclopentyl carbinol, C, 75.68; H, 8.80).

Preparation of Crystalline Derivatives of the **Carbinols.**—Attempts were made to prepare the 3,5-dinitrobenzoate, phenylurethan, and a-naphthylurethan of each carbinol. For the benzoate, half a gram of freshly prepared 3,5-dinitrobenzoyl chloride and a sufficient excess of the carbinol were dissolved in pyridine and heated at 100° for six hours. The solution was then filtered and the filtrate diluted with water until the ester precipitated. It was redissolved in warm 95% ethanol, boiled with finely ground charcoal, allowed to stand for an hour and filtered. Dilution and cooling precipitated the ester from the filtrate. Successive crystallizations were made from warm dilute alcohol.

The urethans were made by adding a sufficient excess of the carbinol to half a gram of the appropriate isocyanate, and heating the mixture in an oil-bath at 150" for six hours or more. The resultant nrethan was dissolved in petroleum ether, filtered, reprecipitated by evaporation and taken up in warm methanol. Further crystallizations were made in the usual manner from either methanol or ethanol.

Summary

Alcohols of a new series, of the type  $\begin{matrix}CH_2-CH_2\\ |\\ CH_2-CH_2\end{matrix}>CH-CHOH-R$ have been prepared and characterized.

A side reaction indicating apparent steric hindrance in the formation of certain cyclic compounds has been studied.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS. VIII. THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF THE ISOMERIC HEPTANES[1]

BY HUGH M. HUFFMAN,[2] GEORGE S. PARKS[3] AND S. BENSON THOMAS[4]

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Recently the nine isomeric heptanes have been prepared in a very pure form by Edgar, Calingaert and Marker.[5] Various physical properties of these samples were subsequently studied by a number of investigators, and much of the resulting data has been discussed and summarized by Edgar and Calingaert.[6] Through the courtesy of Dr. Edgar we have enjoyed the privilege of measuring the heat capacities of these isomers from liquid air temperatures up to that of the room. From the data thus obtained, the corresponding entropies and free energies have been calculated by means of the third law of thermodynamics. The present paper gives the results of our investigation.

In an earlier study dealing with a few isomeric organic compounds, two of us[7] suggested that "in the case of isomers the compound with the lowest melting point has the largest entropy and free energy." The present investigation, as well as the data recently obtained for three isomeric octanes,[8] does not support this suggestion. Rather it appears that in a group of isomers the entropy decreases systematically as the amount of branching increases. Thus the normal compound has always been found to have the largest entropy value. However, in the case of two isomers involving equal amounts of branching, it is usually true that the compound with the lower melting point has the larger entropy. At present no rule

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[1] This paper contains results obtained in an investigation of the heat capacities and free energies of some typical hydrocarbon compounds, listed as Project No. 29 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by The Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[5] Edgar, Calingaert and Marker, THIS JOURNAL, 51, 1483 (1929).

[6] Edgar and Calingaert, *ibid.*, 51, 1540 (1929).

[7] Parks and Huffman, *ibid.*, 48, 2788 (1926).

[8] Parks, Huffman and Thomas. *ibid.*, 52, 1032 (1930).

concerning the free energy of formation of isomers appears universally applicable to all the hydrocarbons and alcohols that have been studied.

Experimental **Results**

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in other places.[9] In view of the accuracy of the various measurements involved and the purity of the several heptane samples, the error in the experimental values is probably less than 1%.

TABLE I

SPECIFIC HEATS

No. 3. 3-Methylhexane: Glass and liquid

Temp., °K.	71.1	74.7	78.0	81.1	84.0	86.9	89.2
C_p per g.	0.178	0.187	0.197	0.205	0.215	0.240	0.362
Temp., °K.	91.0	92.8	95.1	99.1	106.3	118.9	131.4
C_p per g.	0.395	0.397	0.398	0.398	0.400	0.403	0.407
Temp., °K.	151.8	173.8	195.7	219.8	243.1	275.8	289.2
C_p per g.	0.415	0.426	0.440	0.457	0.472	0.498	0.511

No. 4. 3-Ethylpentane: Crystals

Temp., °K.	92.2	98.3	105.0	112.1	118.9	125.2	131.4	137.2
C_p per g.	0.206	0.216	0.227	0.238	0.248	0.259	0.269	0.282

Liquid

Temp., °K.	161.4	166.8	180.4	200.2	217.5	237.5	258.5
C_p per g.	0.416	0.419	0.427	0.442	0.455	0.470	0.486
Temp., °K.	275.4	282.2	287.5	294.8			
C_p per g.	0.499	0.505	0.510	0.519			

No. 5. 2,2-Dimethylpentane: Crystals

Temp., °K.	91.9	97.9	103.3	103.3	111.2	118.4	124.9	131.0
C_p per g.	0.200	0.210	0.219	0.219	0.234	0.249	0.265	0.281

Liquid

Temp., °K.	153.2	154.3	162.2	177.5	186.1	199.8	215.8
C_p per g.	0.388	0.389	0.395	0.407	0.415	0.428	0.442
Temp., °K.	237.4	256.8	275.1	275.1	281.3	287.2	294.1
C_p per g.	0.461	0.478	0.498	0.497	0.505	0.511	0.518

No. 6. 2,3-Dimethylpentane: Glass and liquid

Temp., °K.	68.4	72.8	76.8	80.7	83.3	84.1	86.8	86.9
C_p per g.	0.169	0.177	0.189	0.205	0.252	0.253	0.377	0.377
Temp., °K.	89.2	90.4	92.1	94.2	104.7	111.3	128.0	133.9
C_p per g.	0.376	0.374	0.374	0.376	0.380	0.383	0.389	0.393
Temp., °K.	160.3	181.5	205.0	210.8	234.0	240.1	277.2	291.3
C_p per g.	0.409	0.421	0.437	0.442	0.459	0.465	0.496	0.510

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[9] Parks, THIS JOURNAL., 47,338 (1925); also Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

TABLE I *(Concluded)*

No. 7. 2,4-Dimethylpentane: Crystals

Temp., °K.	91.6	95.1	97.4	104.2	111.6	120.0	129.8	136.3
C_p per g.	0.201	0.209	0.212	0.223	0.237	0.254	0.284	0 313

Liquid

Temp., °K.	160.2	161.2	171.7	181.4	196.3	205.7	215 3	225.7
C_p per g.	0.400	0.402	0.410	0 417	0.430	0.440	0.449	0.458
Temp., °K.	236.4	242 4	261.4	275.4	281 5	288.1	294.4	
C_p per g.	0.468	0.472	0 493	0.505	0 512	0 519	0.527	

No. 8. 3,3-Dimethylpentane: Crystals

Temp., °K.	92.3	97.5	103.7	108.7	114.0	118.2	123.0	128.5
C_p per g.	0.192	0.201	0.212	0.223	0.233	0.243	0.254	0.272

Liquid

Temp., °K.	145.7	151.4	160.7	171.9	183.0	195.5	210.5	225.7
C_p per g.	0.392	0.395	0.400	0.405	0.412	0.421	0.432	0.444
Temp., °K.	239.9	252.7	275.1	280.3	286.5	292.9		
C_p per g.	0.456	0.466	0.486	0.492	0.498	0505		

No. 9. 2,2,3-Trimethylbutane: Crystals I

Temp., °K.	89.5	92.2	94.8	96.7	97.4	99.7	102.8	103.9
C_p per g.	0.212	0.222	0.232	0.242	0.246	0.261	0.330	0.356
Temp., °K.	108.0	109.3	112.2	116.3				
C_p per g.	0.299	0.294	0.298	0.310				

Crystals II

Temp., °K.	129.6	131.2	136.9	148.5	161.8	174.8	187.1	199.1
C_p per g.	0.321	0.324	0.329	0.341	0.354	0.366	0.380	0.391
Temp., °K.	210.7	222.0	230.5	233.6	236.2			
C_p per g.	0.409	0.422	0.431	0.435	0.439			

Liquid

Temp., °K.	253.2	258.5	275.3	275.7	281.6	293.9
C_p per g.	0.459	0.463	0.481	0.479	0.485	0.497

TABLE II

FUSION DATA[a]

No.	Substance	M. p., °K.	Heat of fusion (cal. per g.) 1st result	2nd result	Mean
1	n-Heptane	182.2	33.84	33.73	33.78
2	2-Methylhexane	154.0	21.17	21.16	21.16
4	3-Ethylpentane	154.3	22.47	22.66	22.56
5	2,2-Dimethylpentane	148.1	13.97	13.98	13.98
7	2,4-Dimethylpentane	152.5	16.00	15.94	15.97
8	3,3-Dimethylpentane	138.2	16.83	16.90	16.86
9	2,2,3-Trimethylbutane	247.7	5.18	5.32	5.25

[a] In the calculation of these fusion values, the marked rise in the specific heat of the solid as the melting point is approached was attributed to premelting and the heat absorbed in this region in excess of that obtained by extrapolation of the specific heat data at lower temperatures was added to the heat absorbed at the melting point.

The specific heats and the fusion data, expressed in terms of the 15° calorie[10] and with all weights reduced to a vacuum basis, appear in Tables I and II, respectively. For the sake of spatial economy in Table I, we have omitted the data for n-heptane and 2-methylhexane, as these have been given in an earlier paper.[8] As an illustration of the general character of

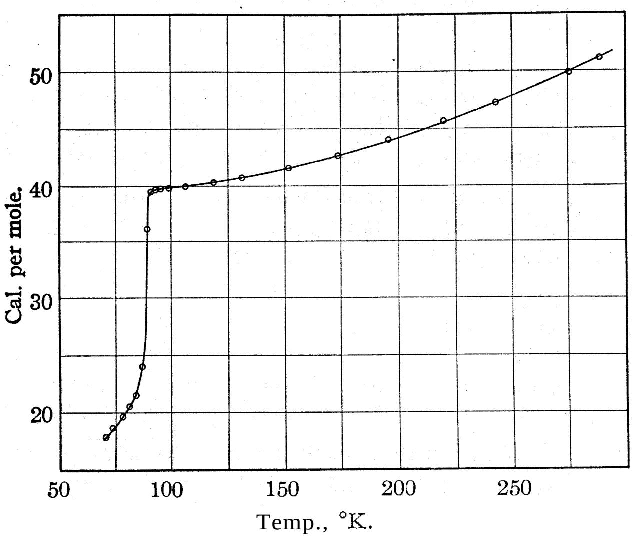

Fig. 1.—The molal heat capacity curve for 3-methylhexane.

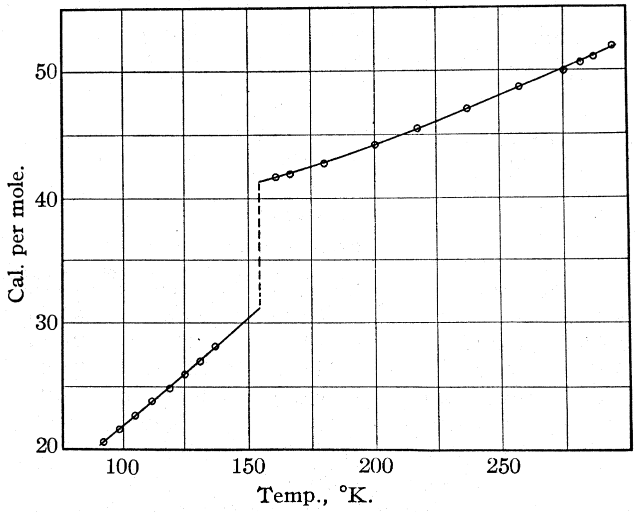

Fig. 2.—The molal heat capacity curve for 3-ethylpentane.

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[10] The factor 0.2390 has been used in converting the results from the joule to the 15° caloric.

the specific heat curves, we have plotted the molal heat capacities of 3-methylhexane and 3-ethylpentane in Figs. 1 and 2.

Two of the heptanes, 3-methylhexane and 2,3-dimethylpentane, failed to crystallize even when slowly cooled to 70°K. These compounds contain asymmetric carbon atoms. However, the liquids studied were optically inactive, being evidently mixtures of the dextro and levo forms in equal amounts. On progressive cooling, they became very viscous and finally solidified to clear glasses at about 100°K. Both substances showed the typical behavior which has been observed with other organic glasses, and the specific heat curves exhibit a 100% increase within a 10° interval.[11]

The last isomer, 2,2,3-trimethylbutane, evidently exists in at least two crystalline forms at low temperatures with a transition point at 121.0°K. The heat of transition was measured and found to be 5.67 cal. per g., a value which slightly exceeds the heat of fusion in magnitude. There was also a marked "hump" or maximum in the heat capacity curve for the low temperature form at about 105°K. The heat effect associated with this hump above the smooth specific heat curve was about 0.58 cal. per g. This particular compound showed no premelting and was apparently very pure.

Discussion

The Heat Capacity Curves.—Recently Andrews[12] has been quite successful in a theoretical analysis of the heat capacity curves for a number of crystalline organic compounds. He considers the values of C_p per mole for benzene, for instance, to be the sum of the energy increments due to intermolecular vibrations, to the various intramolecular vibrations and to the heat absorbed in the expansion of the crystal at constant pressure. The molecule, as a whole, possesses molecular vibrational energy, both translational and rotational, which may be approximately calculated with the aid of the Debye function. Within the benzene molecule the six CH groups possess vibrational energy for three degrees of freedom, which may be estimated by use of Einstein functions. Theoretically there also should be some energy associated with the vibrations of the individual hydrogen atoms, but the binding force of the carbon–hydrogen bond is so great that the magnitude of this vibrational energy is negligible below room temperature. From 0°K. to liquid air temperatures, practically all of the energy absorbed goes into the molecular vibrations. Above 100°K. the energy associated with the oscillations of the CH groups becomes increasingly important, amounting to almost one-half of the total heat capacity at the melting point; likewise, the rate of absorption of heat for the work of expansion, $C_p - C_v$, increases with the temperature, becoming about 10% of the total at 260°K.

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[11] Parks and Huffman, *J. Phys. Chem.*, 31, 1842 (1927).

[12] Andrews, *Chem. Reviews*, 5, 533 (1928).

In the course of our investigations upon these heptanes and other hydro-Carbons, we have applied such theoretical considerations toward an explanation of the heat capacity curves for the crystalline, liquid and glassy states. While we intend to treat the subject from a more quantitative standpoint at a future date, it seems appropriate for us to present our views here in qualitative fashion. For this purpose we have constructed the curves in Fig. 3. The one bearing the label "crystals" represents the theoretical curve for a crystalline heptane, based upon these conceptions of Andrews. It may be considered as the resultant sum of a series of Debye functions (representing the vibrations of the molecule as a whole) and of a series of Einstein functions (representing the various types of vibrations of the several carbon groups in the molecule), there being added, of course, the correction for the $C_p - C_v$ difference.

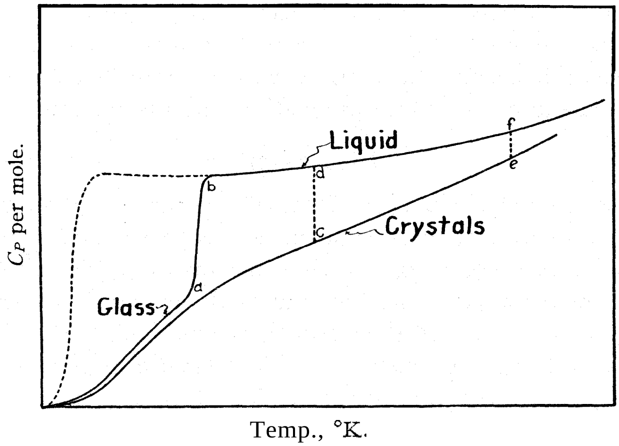

Fig. 3.

We believe that the same type of reasoning can be used to account for the heat capacity curve of a liquid heptane, at least up to room temperature. This amounts to adopting the picture that in a liquid, far below the boiling point, the motion of the molecular units is largely vibrational in character, although undoubtedly these vibrations are more or less anharmonic.[13] As a first approximation the heat capacity curve for such a liquid can be represented, as in the case of the crystalline phase, by the sum of a number of Debye and Einstein functions, in which, however, most of the vibrational frequencies are much lower than for the corresponding crystals, since the cohesive forces are weaker. Assuming for the instant

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[13] Eucken, *Berl.*, Ber., 682 (1914), and Honda, Phil. Mag., 45, 189 (1923), have previously made a similar suggestion to account for the heat capacity of liquid mercury, etc. In this connection see also Eucken, Jette and LaMer, "Fundamentals of Physical Chemistry," McGraw-Hill Book Co., New York, 1925, p. 159.

that the liquid state could be retained even to the lowest temperatures without "hardening" or vitrification, we would expect to obtain a curve somewhat like that labeled "liquid" in Fig. 3. With very low vibrational frequencies the Debye and Einstein functions would first give, at the lowest temperatures, rapidly increasing values which might reach a temporary maximum at, perhaps, 40°K. At still higher temperatures that part of the heat capacity due to the intermolecular vibrations would undoubtedly decrease as the vibrations become more anharmonic and tend to degenerate into translational and rotational motion. On the other hand, the heat capacities associated with some types of intramolecular oscillations certainly do not approach their limiting values below 500 or 600°K. Likewise, the $C_p - C_v$ difference must steadily increase with rising temperature, and this quantity is very considerable for such liquids (10 to 11 cal. per mole for the various heptanes at 293°K.). In view of these several factors the resultant molal heat capacity curve for a liquid heptane would probably flatten out in the neighborhood of liquid air temperatures and then increase but slowly in going up to room temperature.

Of course, the broken portion of the liquid curve is purely imaginary, as every known liquid on cooling either crystallizes or hardens to form a glass. In this connection the production of glasses from such typically non-polar liquids as 3-methylhexane and 2,3-dimethylpentane appears to us especially significant, since heretofore the only organic glasses studied were formed from more or less polar substances, containing carbon, hydrogen and oxygen. In the past the formation of a glass has sometimes been explained by assuming the production of highly associated groups, or even colloidal particles, on cooling the parent liquid. However, the extensive formation of associated groups in the two heptanes just mentioned seems rather improbable, and we believe that the true explanation of the vitrifaction of a liquid is to be found in a great increase, within a relatively small temperature interval, of the cohesive forces acting between the molecules.[14] As a result of this increase in cohesion, there should also be a marked increase in the vibrational frequencies for the oscillations of the molecular units and for the intramolecular oscillations of the individual carbon atoms along certain axes of motion; hence, in accordance with the Debye and Einstein functions, the resultant molal heat capacity might be expected to fall off rapidly within a small temperature interval. Experimentally this rapid change has been found for all organic glasses so far studied; it is indicated graphically by the line ab in Fig. 3. Since the glassy form of a substance

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[14] This increase in the cohesive forces is probably the result of the volume shrinkage in the liquid, consequent to a decrease of the thermal motions with lowering of temperature. That such a change in cohesion takes place is evidenced by the tremendous increases in the viscosity of the parent liquid just above the "hardening point"—increases of a hundred-fold or more within ten degrees, Parks and Gilkey, J. *Phys. Chem.*, **33, 1432** (1929).

ordinarily exhibits a heat capacity curve similar to but slightly above that for the crystalline form, it would seem that the cohesive forces, or internal pressures, in the two forms must be of about the same magnitude. In fact, we may picture the glassy and crystalline states as containing essentially the same units and as held together by essentially the same forces, the former merely lacking the regularity of arrangement of these units and forces found in the latter.

If the foregoing explanation for the formation of a glass be valid, we might expect that certain soft crystals, showing a large coefficient of thermal expansion and differing but slightly in energy content from the corresponding liquid form, might undergo a similar large change in internal cohesive forces and consequently a rapid fall in heat capacity within a brief temperature interval. In this connection it is interesting to note that Kelley[15] has studied such a substance in the form of the high-temperature modification of cyclohexanol and has observed a sharp drop in its heat capacity curve about 90° below the point of transition into the low-temperature modification.

Finally we might call attention to the significance of the lines cd and ef in the diagram. If the crystalline heptane be one which melts at a low temperature such as c, there should be a decided increase in heat capacity after fusion, the change being measured by the length of cd. On the other hand, if fusion takes place at a relatively high temperature e, the increase in specific heat should be small. These deductions are in agreement with the experimental data.

Entropies of the Heptanes.—Using our specific heat and fusion data in conjunction with the third law of thermodynamics, we have calculated the molal entropies at 298.1°K. for the seven heptanes which crystallized. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman[16] for estimating the entropy increases for the crystals (Col. 3 of Table III) from 0 to 90°K. The various entropy increments from 90 to 298°K., which appear in Cols. 4, 5 and 6 of the table, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree appear under the heading "S_{298} experimental" in the seventh column; they are probably accurate to within 1%.

Although the third law of thermodynamics is not strictly applicable to non-crystalline substances, we have roughly estimated the entropies of 3-methylhexane and 2,3-dimethylpentane. In these instances we obtained graphically the entropy increment of the glass and liquid between 70 and 298.1°K. (Col. 6 of Table III). By comparison with the other heptanes we then estimated the increment between 0 and 70°K. and to this result we

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[15] Kelley, THIS JOURNAL, 51, 1402 (1929).

[16] Kelley, Parks and Huffman, *J. Phys. Chem.*, 33, 1802 (1929).

TABLE III

ENTROPIES OF THE HEPTANES PER MOLE

No.	Substance	Crystals 0–90°K.	Crystals Above 90°K.	Fusion	Liquid	S_{298} Experimental	S_{298} Predicted
1	*n*-Heptane	16.97	18.80	18.58	24.51	78.9	78.9
2	2-Methylhexane	16.76	13.92	13.75	30.86	75.3	74.4
3	3-Methylhexane	16.9[a]	...	...	57.15	74.0	74.4
4	3-Ethylpentane	16.46	13.47	14.63	30.09	74.6	74.4
5	2,2-Dimethylpentane	15.32	12.33	9.44	30.97	68.1	69.9
6	2,3-Dimethylpentane	16.6[a]	...	...	56.60	73.2	69.9
7	2,4-Dimethylpentane	15.75	13.14	10.48	30.37	69.7	69.9
8	3,3-Dimethylpentane	14.50	9.94	12.21	33.45	70.1	69.9
9	2,2,3-Trimethylbutane	14.0	39.79[b]	2.11	8.86	64.8	65.4

[a] This is the estimated value for the entropy of the glass at 70°K. [b] This value includes 4.67 E. U. for the transition at 121.0° and 0.55 E. U. for the entropy of the hump at 105°K.

added 4 E. U. for the entropy of the glass at the absolute zero. The whole procedure, while somewhat arbitrary, probably does not involve an error greater than 2.5 E. U. in the value below 70°, since Kelley[17] has recently shown that several organic glasses apparently have entropies between 2.6 and 4.6 E. U. at 0°K. The resulting values for S_{298} are probably accurate to within 3.0 E. U.

In a previous paper it was shown that the entropy of a liquid paraffin hydrocarbon could be calculated quite accurately by the equation, $S_{298} = 25.0 + 7.7n - 4.5r$, where n is the number of carbon atoms in the molecule and r represents the number of branches on the straight chain. In the present study we have again used this equation to obtain the values for "S_{298} predicted" in the last column of Table III. On the whole the predicted values are in very good agreement with the experimental results.

The Free Energies of the Heptanes.—We have also calculated the free energies of formation of these heptanes by means of the fundamental thermodynamic equation, $\Delta F = \Delta H - T\Delta S$.

The essential data are given in Table IV. The heats of combustion at constant pressure appear in Col. 3; they were recently determined by the U. S. Bureau of Standards[18] at 20° and have been recalculated to 25° for our present purpose. The various results are probably accurate to about 1000 cal. and indicate that the molal heats of combustion of these isomers are practically identical. The ΔH_{298} values were then calculated by use of 68,330 and 94,270 cal.[8] for the heats of combustion of hydrogen and graphitic carbon, respectively. Column 5 contains the entropy of formation of each compound, which is simply the difference between its S_{298} and the corresponding values for the entropies of the elements contained therein. For

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[17] Kelley, THIS JOURNAL, 51, 785 (1929).

[18] Kharasch, Bur. *Standards J. Research*, *2*, 359 (1929).

this purpose the respective entropies of carbon and hydrogen were taken as 1.3 and 14.8 E. U. per gram atom.[8]

TABLE IV

THERMAL DATA AT 298.1°K.

(The 15° cal. is used throughout and all weights have been reduced to a vacuum basis)

No.	Substance	Heat of combustion at constant pressure	ΔH_{298} Cal.	ΔS_{298} E. U.	ΔF_{298} Cal.
1	n-Heptane	1,149,400	−57,100	−167.0	−7300
2	2-Methylhexane	1,148,400	−58,100	−170.6	−7200
3	3-Methylhexane	1,148,400	−58,100	−171.9	−6800
4	3-Ethylpentane	1,149,400	−57,100	−171.3	−6000
5	2,2-Dimethylpentane	1,147,400	−59,100	−177.8	−6100
6	2,3-Dimethylpentane	1,148,400	−58,100	−172.7	−6700
7	2,4-Dimethylpentane	1,148,400	−58,100	−176.2	−5600
8	3,3-Dimethylpentane	1,147,400	−59,100	−175.8	−6700
9	2,2,3-Trimethylbutane	1,147,400	−59,100	−181.1	−5100

The molal free energies appear in the last column of the table. As calculated from the individual heats of combustion the nine values lie very close together, the maximum difference being 2200 cal. between *n*-heptane and 2,2,3-trimethylbutane. However, if the heats of combustion of the isomers are assumed to be identical and 1,148,400 cal. per mole, the free energies of n-heptane and 3-ethylpentane will be lowered by 1000 cal., while the values for 2,2-dimethylpentane, 3,3-dimethylpentane and 2,2,3-trimethylbutane will be raised algebraically by an equal amount. The free energy difference between compounds 1 and 9 will then become 4200 cal.

In any event it is clear that increased branching among these isomers leads to a small increase in the free energy level. Taking the values as given in the table, we find that the effect of shortening the main chain by introducing side branches is to raise the free energy level by an average of 600 cal. per branch. This result, while small, agrees fairly well with the 900 cal. average for a similar change in the three octane isomers previously studied by the authors. In each instance it thus appears that the normal paraffin is thermodynamically the most stable in its group.

Before concluding we wish to thank Dr. Graham Edgar, Director of the Research Laboratory of the Ethyl Gasoline Corporation, for the loan of these hydrocarbon samples and for his encouragement in this research.

Summary

1. The heat capacities of the nine isomeric heptanes have been measured between liquid air temperature and that of the room.

2. A qualitative explanation of the typical heat capacity curves for the crystalline, glassy and liquid states has been suggested.

3. The entropies of the isomeric heptanes have been calculated from the heat capacity data. These results agree well with the values predicted by means of a simple, empirical equation.

4. The corresponding free energies have also been calculated. It appears that with increased branching in this group of heptane isomers the free energy level is raised by an average of 600 cal. for each side branch.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE RICE INSTITUTE]

ALPHA-TETRAHYDROFURFURYL CHLORIDE AND ALPHA-TETRAHYDROFURFURYL ETHERS

BY W. R. KIRNER

RECEIVED MARCH 31, 1930 PUBLISHED AUGUST 5, 1930

In a recent paper from this Laboratory[1] the synthesis of α-furfuryl chloride and a few a-furfuryl ethers was described. The preparation of tetrahydrofurfuryl chloride has now been accomplished by a similar application of the Darzens reaction to tetrahydrofurfuryl alcohol. This alcohol is now available in quantity from the Miner Laboratories of Chicago. Furfuryl chloride was found to be a relatively unstable substance having a sharp odor and exhibiting lachrymatory properties and possessing an extremely reactive chlorine atom. Tetrahydrofurfuryl chloride, on the other hand, is a relatively stable substance with a mildly pleasant odor, exhibits no lachrymatory properties and has an extremely unreactive chlorine atom.

The synthesis of the tetrahydrofurfuryl ethers was first attempted by the method which was successfully used for the preparation of the furfuryl ethers, namely, treatment of the chloride with the desired alcohol in the presence of pulverized potassium hydroxide. Treatment of furfuryl chloride under these conditions gave high yields of ethers with the reaction occurring very rapidly. In the case of the tetrahydrofurfuryl chloride this method failed. It was found that the chlorine atom in tetrahydrofurfuryl chloride was very much less reactive than the chlorine atom in furfuryl chloride. Thus, in an attempt to prepare tetrahydrofurfuryl methyl ether, tetrahydrofurfuryl chloride was treated with pulverized potassium hydroxide and absolute methyl alcohol and refluxed for a considerable period of time at the boiling point of the alcohol. The reaction occurred extremely slowly and only to a slight extent. It is possible that this reaction might be used for the preparation of the higher ethers for then the reaction could be carried out at a much higher temperature than is possible when methyl alcohol is used. However, this proposed method of preparation of the tetrahydrofurfuryl ethers has the disadvantage that an unsaturated tetrahydrofuran derivative can be formed simultaneously due to the elimination of halogen acid by the basic reagent used, a reaction which was not possible in the case of furfuryl chloride. Thus

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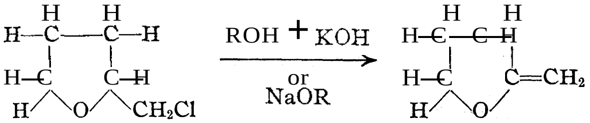
[1] Kirner, THIS JOURNAL, 50, 1955 (1928).



In fact, the small amount of impure ether which was isolated in the above mentioned experiment showed strong reducing action to both bromine and potassium permanganate and obviously contained an unsaturated compound. Work on this phase of the reaction is being continued with the object of isolating the unsaturated compound in a pure state.

The synthesis of the ethers was satisfactorily accomplished using the method described by Wissell and Tollens[2] for the synthesis of the furfuryl ethers. This consisted in treating tetrahydrofurfuryl alcohol with the desired alkyl halide in the presence of pulverized potassium hydroxide. The reaction took place smoothly and rapidly and gave excellent yields. The tetrahydrofurfuryl ethers are much more stable than the simple furfuryl ethers and remain practically colorless when merely placed in glass-stoppered bottles under atmospheric pressure and in the absence of a stabilizing agent such as hydroquinone. Table I lists the physical properties, yields and analytical data of the chloride and the ethers which were prepared.

In comparing the boiling points of the furfuryl and tetrahydrofurfuryl compounds it is found that the tetrahydrofurfuryl compounds boil uniformly about 6° higher than the corresponding furfuryl compounds. The densities and refractive indices of the tetrahydro compounds are lower than those of the corresponding furfuryl compounds. In the case of the furfuryl compounds the molecular refraction showed a slight depression,

TABLE I

DATA ON TETRAHYDROFURFURYL COMPOUNDS

No.	Tetrahydrofurfuryl	B. p., °C.	Pressure, mm.	Yield, %
1	Chloride	149.0–149.5	721	75
		38.5–39	10	
2	Methyl ether (methyl iodide method)	140–141	715.5	73
2a	Methyl ether (dimethyl sulfate method)	140–141.5	723	74
3	Ethyl ether	152–154	726	85
4	*n*-Propyl ether	175–176.5	728	86
5	*n*-Butyl ether	194.5–196	721	79
6	Iso-amyl ether	86.5–87.5	10	69
		209–210 (corr.)	718	
7	n-Hexyl ether	107.5–108.5	10	63
		231–233	708	
8	Allyl ether	179.5–181	707	83
9	Benzyl ether	141.5–143	10	92

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[2] Wissell and Tollens, Ann., 272,291 (1892).

TABLE I *(Concluded)*

No.	$n_D^{20°}$ (Abbé)	d_4^{20}	d_{20}^{20}	Mol. refr. (M_D) Calcd.	Obs.
1	14560	11102	1.1133	29.60	29.51
2	1 4292	0 9640	0 9667	30.99	31 06
2a	1 4300	.9625	.9653	30.99	31.16
3	1.4298	.9386	9412	35 61	35.80
4	1.4313	.9248	.9274	40.23	40.36
5	1.4357	.9150	.9176	44.85	45.16
6	1.4370	.9040	.9065	49.47	49.89
7	1.4407	.9019	.9045	54.08	54.47
8	1.4498	.9571	.9598	39.76	39.89
9	1.5174	1.0484	1.0514	55.10	55.47

ANALYSES

No.	Sample, mg.	CO_2, mg.	H_2O, mg.	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
1	4 092	7.520	2 78	49 78	53 12	7 53	7 60
2	4 590	10.440	4 13	62 02	62 03	10 42	10.07
3	4 236	10.040	3 96	64 56	64 64	10 84	10.46
4	5 380	13.160	5 30	66 61	66 71	11.19	11.02
5	5 524	13.855	5 57	68 29	68.40	11 47	11.28
6	4 860	12.460	503	69.70	69.92	11.71	11 58
7	5 244	13 600	5 50	70 90	70 73	11.91	11.73
8	5 712	14 160	4 98	67 55	67 61	9 93	9 75
9	4 541	12 540	328	7495	7531	8.39	8.08

whereas with the tetrahydrofurfuryl compounds there appears to be a slight exaltation.

An attempt was made to prepare tetrahydrofurfuryl iodide by treatment of the chloride with sodium iodide in acetone solution. The mixture was refluxed for about thirty-five hours and allowed to stand for two and one-half months. Only a very small amount of sodium chloride precipitated and on working up the mixture practically all of the chloride was recovered unchanged; a small amount of higher-boiling residue remained which was possibly the iodide. This experiment confirms the non-reactivity of the chlorine atom previously mentioned.

Dr. Irvine Page, director of the Chemistry Division of the Deutsche Forschungsanstalt für Psychiatrie of the Kaiser Wilhelm Institut in Munich, kindly made a preliminary study of the physiological activity of the tetrahydrofurfuryl ethers on mice and guinea pigs. He reported the ethers moderately toxic, the M. L. D. for the ethyl and propyl compounds on both mice and guinea pigs being about 0.14 cc. per kilo body weight when injected intravenously and 1.4 cc. per kilo body weight when injected intraperitoneally, these values decreasing with the higher ethers. Subcutaneous injection seemed to produce little effect. Injection of the substances intraperitoneally first caused muscular incoordination and then complete muscular relaxation with a semi-anesthetic stage in which the animals showed diminished pain sensibility and reflexes, the condition somewhat resembling twilight sleep. After one to two hours the animals appeared quite normal. Autopsies after injection of toxic doses showed chemical peritonitis. The anesthetic action appeared to increase from the methyl to the butyl compound (in the latter compound 0.8 cc. in a guinea pig weighing 680 g. caused total anesthesia lasting for nine hours), and then decreased again in the higher ethers. The benzyl ether was found to be quite toxic and the animals showed signs of central nervous system irritation. In this case the anesthetic action was light. In many cases the animals recovered from the anesthetic action but died later, death being due to intestinal necrosis rather than to an inherent toxicity in the compounds themselves.

It is a pleasure to acknowledge my thanks to Dr. Page for his kindness in carrying out the pharmacological investigation on these compounds as well as for the use of the refractometer with which the refractive indices were measured. I also wish to express my appreciation to Professor Heinrich Wieland for granting me permission to carry out this work in the Staats Laboratorium in Munich.

Experimental

I. Preparation of **α-Tetrahydrofurfuryl Chloride.**—A 200-cc. round-bottomed three-necked flask was fitted with a mechanical stirrer in the center neck; a 50-cc. dropping funnel (which had its delivery tube bent so as to deliver its contents near the center of the flask), was fitted into one side neck and a 50° thermometer was fitted into the remaining side neck. Fifty-one grams (0.5 mole) of freshly distilled tetrahydrofurfuryl alcohol and 43.5 g. (0.55 mole) of pyridine were placed in the flask; 65.5 g. (0.55 mole) of thionyl chloride (which was distilled from linseed oil and was perfectly water-white) was placed in the dropping funnel and added dropwise to the rapidly stirred alcohol–pyridine mixture. A vigorous reaction occurred with rise of temperature and darkening of the reaction mixture. The rate of addition of the thionyl chloride was such that addition was completed in approximately one and one-half hours; the temperature rose to between 50–55°. At the end of thirty to forty minutes a pasty, crystalline mass began to separate, which finally became so thick that the stirrer had difficulty in moving it. To avoid the thionyl chloride dropping on one spot of this mass, it was found that by gently tapping the flask with the hand the mass was loosened sufficiently so that it slowly rotated. At the end of about one and one-quarter hours this crystalline mass had redissolved leaving a dark brown liquid.

After the thionyl chloride was all added stirring was continued. As the temperature decreased crystallization again occurred and stirring was continued until this was complete and then the mixture was allowed to stand overnight. If crystallization occurred when the stirrer was not in motion it was found difficult to remove the stirrer from the hard crystalline mass which filled the flask the next morning.

The stirrer, dropping funnel and thermometer were removed and the liquid present in the flask was decanted off into an Erlenmeyer flask. The crystalline residue was then broken up, first with a sharp-pointed file and then with a glass rod having a button-shaped end; this treatment leaves a dark brown pasty mass of crystals. These were extracted by decantation seven times with 25-cc. portions of dry ether, the ether extracts being added to the solution originally decanted from the crystals. This combined solution was then washed three times with 50-cc. portions of water and allowed to dry over anhydrous sodium sulfate. The ethereal solution had a light brown color. The crystalline residue may be dissolved in water and treated with alkali to recover the pyridine.

The ether was distilled off and the residue fractionated in vacuum from a Claisen fractionating flask, the side arm of which was fitted with a short water condenser. The chloride distilled steadily at 41.5–42° at 11 mm. The boiling point observed at other pressures was 44–44.5" at 13 mm., and 45° at 14 mm. The yield of pure, distilled product was 75% and was duplicated many times. The remaining physical properties and analytical data are given in Table I. The chloride was a perfectly water-white liquid with a peculiar characteristic odor, but not at all lachrymatory as in the case of furfuryl chloride. It was found to be much more stable than furfuryl chloride and remained water-white for a long period when merely placed in a glass-stoppered bottle.

Attempts were also made to prepare the chloride by the use of phosphorus trichloride. The alcohol was dissolved in anhydrous ether and treated dropwise with a 10% excess of phosphorus trichloride, also dissolved in anhydrous ether. In one experiment the reaction mixture was kept cold; in another the reaction was run at the boiling point of the ether and in a third case a molecular quantity of pyridine was present. The yield by all of these methods was approximately 15% and in the fractional distillation there was always a considerable amount of high-boiling residue which was presumably unreacted alcohol. The chloride prepared by these methods always turned dark in a few days and gave off hydrogen chloride, the decomposition occurring more slowly, however, in the product obtained from the pyridine reaction. The phosphorus trichloride method is very much inferior to the thionyl chloride method both from the standpoint of yield and purity of the product obtained.

II. Preparation of **α-Tetrahydrofurfuryl** Ethers.—In general, about 0.3 mole of **tetrahydrofurfuryl** alcohol was mixed with a 200% excess of the desired bromide (except in case of the benzyl compound, where the chloride was used, and in case of the methyl compound, where the iodide was used), in a 250-cc. round-bottomed flask and then 100% excess of pulverized potassium hydroxide was added in small portions. Considerable heat was evolved, particularly in the case of the more reactive halides such as methyl iodide, ethyl and allyl bromide and benzyl chloride; when volatile halides were used the reaction mixture had to be cooled to avoid loss of the halide. The sodium halide precipitated voluminously during the addition of the alkali. When the potassium hydroxide was all added, the mixture was heated in a water-bath for three hours at such a temperature that the lower alkyl halides refluxed; for the higher alkyl halides a boiling water-bath was used. In the reactions involving the lower alkyl halides the excess alkyl halide was distilled off through a goose-neck tube at the end of the refluxing period, cooled, and 75 cc. of water added to the residue; in case of the higher alkyl halides water was added directly after being refluxed and cooled. The oily layer which separated was removed with a separatory funnel and the aqueous layer extracted three times with 25-cc. portions of ether. (The methyl ether is considerably soluble in water and no layer separated on adding water; therefore seven extractions with 25-cc. portions of ether were made.) The combined oily layer-ethereal solution was washed twice with 50-cc. portions of a saturated solution of sodium sulfate and the ethereal solution dried over anhydrous sodium sulfate. After standing overnight the solution was filtered from the sodium sulfate, the ether distilled off and the residue fractionated from a Claissen fractionating flask. In the case of the iso-amyl, n-hexyl and benzyl ethers the fractionation was performed in vacuum; in the other cases at atmospheric pressure. Before measuring the physical properties of the ethers they were allowed to stand over metallic sodium and then redistilled. All of the ethers showed considerable evidence of reaction with the sodium but without appreciable evolution of hydrogen. The tetrahydrofurfuryl ethers are all stable, water-white liquids with extremely pleasant odors. The physical constants, yields and analytical data are given in Table I.

The tetrahydrofurfuryl methyl ether was also made by methylation of the alcohol with dimethyl sulfate. A 100% excess of 40% sodium hydroxide solution was placed in a three-necked flask fitted with a stirrer and two dropping funnels and cooled in an ice-bath. The tetrahydrofurfuryl alcohol and a 50% excess of dimethyl sulfate were added simultaneously, dropwise, from the funnels, the reaction mixture being kept cold, and the temperature of the mixture not rising above 8°. After addition of the liquids was complete the mixture was stirred for three and one-half hours while cooled, and a further two and one-half hours with the ice-bath removed and then allowed to stand overnight at room temperature.

The reaction mixture consisted of two layers: an upper oily layer and the lower aqueous–alkaline layer. The mixture was transferred to a 250-cc. round-bottomed flask and steam distilled. The distillate at first contained two layers, but due to the solubility of the methyl ether in water, the insoluble layer gradually dissolved as more and more water distilled. The distillate was saturated with potassium carbonate, which caused an oily layer to separate, and was removed and then the aqueous layer was extracted three times with 25-cc. portions of ether. The combined solution was then dried over anhydrous potassium carbonate. The solution was filtered from the drying agent, the ether distilled off and the residue fractionated. The product obtained by this method, after being dried over metallic sodium and redistilled, agreed satisfactorily in its physical properties and in yield with that obtained by the methylation of tetrahydrofurfuryl alcohol with methyl iodide.

Summary

1. Tetrahydrofurfuryl chloride has been prepared using the Darzens reaction on tetrahydrofurfuryl alcohol and its physical properties determined. This chloride is much more stable and less reactive than furfuryl chloride.

2. The following tetrahydrofurfuryl ethers have been prepared by alkylation of tetrahydrofurfuryl alcohol, characterized and a preliminary study made of their physiological activity: methyl, ethyl, n-propyl, n-butyl, iso-amyl, n-hexyl, allyl and benzyl. The methyl ether was prepared by alkylation with both methyl iodide and dimethyl sulfate. These ethers are considerably more stable than the corresponding furfuryl ethers.

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[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXIX. THE CONSTITUTION OF ALKALI CELLULOSE[1]

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Introduction

The determination of the composition of the solid phase when cellulose is brought into contact with solutions of sodium hydroxide of varying concentrations has been the subject of numerous researches extending over a period of more than eighty years.

The main purpose of this investigation is to show whether the effect is chemical, physical or physico-chemical, or due to a combination of these possibilities.

As early as 1844 Mercer[4] assumed that a chemical compound was formed between the cellulose and sodium hydroxide at a certain optimum concentration. This idea received experimental support from the researches of Gladstone,[5] Thiele,[6] Vieweg,[7] Lindemann,[8] Normann,[9] Traube[10] and Hess.[11] Other more recent investigators include d'Ans and Jaeger,[12] Dehnert and Koenig,[13] Heuser and Niethammer,[14] Heuser and Bartunek,[15] Karrer[16] and Liepatow.[17]

A thorough review of the literature is to be found in papers by Blanco[18] and Clibbens.[19] Gladstone,[5] Karrer,[16] Hiibner and Teltscher,[20] Heuser

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[1] Contribution from the Department of Industrial and Cellulose Chemistry, McGill University, Montreal, Canada, with financial assistance from the Canadian Pulp and Paper Association.

[2] Research Fellow, Pulp and Paper Research Institute, Montreal.

[3] Professor of Industrial and Cellulose Chemistry. McGill University, Montreal.

[4] J. Mercer, English Patent, **13,296 (1850).**

[5] J. H. Gladstone, **J.** *Chem. Soc.*, 5, **17 (1852).**

[6] E. Thiele, *Chem.-Ztg.*, 25, **610 (1901).**

[7] **W.** Vieweg, *Ber.*, 40, **3876 (1907).**

[8] **O. K.** Lindemann, "Dissertation," Dresden, 1909.

[9] W. Normann, *Chem.-Ztg.*, 30, 584 **(1906).**

[10] **W.** Traube, *Ber.*, 55, **1899 (1922).**

[11] **K.** Hess, *Ann.*, 435, **1 (1923);** *Z. angew. Chem.*, 38, **320 (1925).**

[12] **J.** d'Ans and *A.* Jaeger, *Cellrlosechemie,* 6, **137 (1925).**

[13] F. Dehnert and W. Koenig, *ibid.*, 5, 107 **(1924); 6, 1 (1925).**

[14] E. Heuser and W. Niethammer, *ibid.*, 6, **13 (1925).**

[15] E. Heuser and L. Bartunek, *ibid.*, 6, **14 (1925).**

[16] P. Karrer, *ibid.*, 2, **124 (1921).**

[17] S. Liepatow, **J.** *Russ. Phys.-Chem. Soc.*, 57, *48* **(1925).**

[18] **G. W.** Blanco, *Ind. Eng. Chem.*, 20, **926 (1928).**

[19] **D. A.** Clibbens, **J.** *Text. Inst.*, 14, T217 **(1923).**

[20] J. Hubner and F. Teltscher, **J.** *Soc. Chem. Ind.*, *28,* **641 (1909).**

and Niethammer[14] and Rassow and Wadewitz[21] attempted to wash the soda cellulose free from adhering alkali with alcohol. In the first two instances, the existence of a compound $(C_6H_{10}O_5)_2\cdot NaOH$ is claimed, while the other workers find the method unsatisfactory.

Vieweg[7] initiated the "indirect method," namely, the evaluation of data obtained from titration of the final equilibrium solutions.

It was found that a decrease in the alkali concentration always took place, and from this Vieweg calculated the absorption. From the data he concluded that the existence of two compounds was proved, *viz.* $(C_6H_{10}O_5)_2\cdot NaOH$ and $(C_6H_{10}O_5)_2\cdot 2NaOH$.

Similar investigations have been carried out with various modifications by Heuser,[14,15] Miller,[22] Joyner,[23] Dehnert and Koenig,[13] Karrer and Nishida,[24] Liepatow,[17] d'Ans and Jaeger,[12] Kolthoff,[25] Rumbold[26] and others.

Dehnert and Koenig,[13] as well as d'Ans and Jaeger,[12] also confirmed the formation of Vieweg's second compound at high alkali concentrations, while Karrer,[16] Hess,[11] Heuser and his co-workers[14,15] deny this.

From a consideration of the various curves obtained by using the "indirect method," in which concentrations of sodium hydroxide solution were plotted against weight of sodium hydroxide removed, the weight of evidence seems to show that there is some abnormal condition prevailing where the discontinuities of the curves occur. However, in all of these investigations, little or no attention has been paid to the absorption of water by the cellulose. Unless this takes place in constant amount, or in quantities so small that the effect would not be noticed, no definite conclusions can be drawn from the absorption curves obtained.

Leighton,[27] and Coward and Spencer," used a centrifugal method to remove superfluous sodium hydroxide, in this way claiming to separate the amount of absorbed water from that of the absorbed or combined alkali. From their results they conclude that the phenomenon is due to absorption. Nevertheless the weight of evidence from other sources, as well as that obtained by most investigators using the "indirect method," tends to strengthen the belief that a chemical compound is formed.

Although the alcohol washing method, as developed by various investigators, has not led to definite conclusions as to the nature of the absorption process, the authors believe that the fault lies for the most part in its application rather than in an inherent inconsistency of the method.

[21] B. Rassow and M. Wadewitz, *J. prakt. Chem.*, 106, 266 (1923).

[22] O. Miller, *Ber.*, 40,4903 (1907); 41,4292 (1908); 43,3430 (1910); 44,728 (1911).

[23] R. A. Joyner, *J. Chem. Soc.*, 121, 2395 (1922).

[24] P. Karrer and K. Nishida, *Cellulosechemie*, 5, 69 (1924).

[25] I. M. Kolthoff, *Pharm. Weekblad.*, 58, 46 (1921).

[26] J. A. Rumbold, THIS JOURNAL, 52, 1013 (1930).

[27] A. Leighton, *J. Phys. Chem.*, *20*, 32 (1916).

[28] H. F. Coward and L. Spencer, *J. Text. Inst.*, *14*, *T32* (1923).

With this idea in view a systematic method of attack has been developed which seems to lead to consistent and comprehensible results.

Experimental Procedure

After immersion of the cotton cellulose in sodium hydroxide solution under conditions which will be described later, the sample was removed by means of a glass rod and filtered under suction in a Buchner funnel. The wet mass was well pressed by a flattened glass rod for three minutes, at the end of which period it was quickly transferred to a beaker containing 100 cc, of 95% alcohol, with which it was thoroughly mixed for two minutes.

The supernatant liquor was poured off into a dry flask and most of the solution pressed out of the cotton by means of a flattened glass rod, the operation requiring one minute. The washed fiber was then placed under suction, where it was pressed carefully for one minute and allowed to stand under suction for one minute longer. At the end of this time the material was again transferred to 100 cc. of alcohol, agitated for two minuter (not sufficiently vigorously to break up the fiber), pressed for one minute, the liquid collected and again placed under suction. This process was repeated for every washing.

An aliquot portion of each of the washing solutions was then transferred to a beaker, the alcohol removed by gentle boiling, and the alkali present determined by titration against standard sulfuric acid using methyl orange as indicator. The removal of alcohol by boiling eliminated the indicator difficulties experienced by Heuser.[14] After completing the last washing the cotton was stirred with distilled water and titrated with acid to determine the remaining alkali.

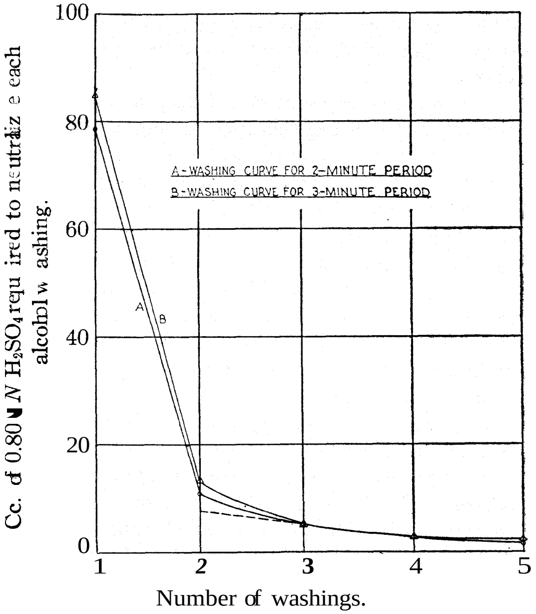

Fig. 1.

Repeated experiments showed that this method gave reproducible results, and established the fact that variations in the method, such as washing for a longer time, or with different amounts of alcohol, gave the same final result.

The following data (shown in Fig. 1) illustrate the calculation of the results.

Initial strength of sodium hydroxide solution = 23.2% by weight; washing period two minutes.

No. of washing	1	2	3	4	5
0.807 N H_2SO_4 required to neutralize each washing, cc.	78.6	10.82	5.14	2.77	1.65

Equiv. of alkali remaining in the cellulose = 22.10 cc. Extrapolated value to the *second* washing from Graph (I) 7.5 cc.

Then 22.10 + 7.50 + 5.14 + 2.77 + 1.75 = 39.16 cc. of 0.807 N acid are equivalent to the caustic alkali directly associated with 4.332 g. of cellulose, *i. e.*, 29.3 g. of NaOH to 100 g. cellulose.

For a washing period of three minutes the value found was 29 5 g. of NaOH per 100 g. of cellulose.

The agreement is within the limit of experimental error. Similar agreement was obtained when 150 cc. of alcohol, instead of 100 cc., was used for the washing. Therefore the conclusion was reached that the method could be applied to determine the amount of alkali combined with, or absorbed in, the fiber.

The absorption experiments were carried out at 25±0.02° in a water thermostat. For the absorption vessel a cylindrical glass jar of about 300 cc. capacity was used, which was coated internally with a thin layer of paraffin wax and fitted with a rubber stopper provided with an exit tube and a tube dipping nearly to the bottom of the vessel.

During an experiment, nitrogen was bubbled gently through the mixture of cellulose and alkali to ensure thorough mixing, and to prevent oxidation and the absorption of carbon dioxide. The gas was passed through sodium hydroxide solution of the same strength as that contained in the experimental vessel in order to remove all carbon dioxide.

Pure "absorbent cotton" was used in these experiments. The a-cellulose value was 99.1%, the ash 0.05%. Before use it was dried in a vacuum for six hours at 60–70° and kept in a vacuum desiccator over phosphoric anhydride.

The sodium hydroxide was Schuchardt's, purified by means of alcohol; 1 kg. was dissolved in 1 liter of water and allowed to stand for ten days. The clear liquid was then forced out of a delivery tube, by means of carbon dioxide-free air, into a measuring cylinder, from which it was transferred in the same way to a flask containing the appropriate volume of air-free water. It was then a simple matter to fill a pipet with the carbonate free solution, and to transfer it to the reaction vessel. In this way a soda solution containing less than 1 part in 600 of carbonate was prepared.

The determination of the indirect absorption was carried out as follows. Dry cellulose (5 g.) was accurately weighed out and placed in the vessel, and 75 cc. of the sodium hydroxide solution added, during the passage of a slow stream of nitrogen. The concentrations of the initial and final solutions were determined, and from the difference between these at equilibrium, values for the indirect absorption were calculated according to Vieweg's procedure.

The cellulose was allowed to remain in contact with the soda solution for four hours, an interval of time which in the experience of other workers, *e.* g., Miller,[22] would appear to be ample time for equilibrium to be established.

The wet fiber was then dried for three minutes using suction and subjected to a washing process at the end of which the residual alkali was found by titration. Thus it was possible to calculate a value for the alkali directly associated with the fiber over a wide range of concentrations according to the method of alcohol washing which has been outlined.

The results for the absorption as determined by the Indirect and Direct Methods are included in Table I.

Discussion of Results

The Method of Washing.—A consideration of the alcohol washing diagrams, Fig. 1, shows that undoubtedly the sodium hydroxide associated

TABLE I

ABSORPTION RESULTS

Init. concn. of NaOH in g./100 g. of soln.	"Indirect Detn.," g. of NaOH/100 g. of cellulose	Direct Detn., g. of NaOH/100 g. of cellulose	Init. concn. of NaOH in g./100 g. of soln.	"Indirect Detn.," g. of NaOH/100 g. of cellulose	Direct Detn., g. of NaOH/100 g. of cellulose	Init. concn. of NaOH in g./100 g. of soln.	"Indirect Detn.," g. of NaOH/100 g. of cellulose	Direct Detn., g. of NaOH/100 g. of cellulose
0.32	0.7	1.1	13.4	13.0	25.7	232	18.2	29.5
0.85	1.0	...	14.15	128	25.6	25.1	19.7	31.7
2 05	0 9	1 7	14.15	12 9	25.3	26.25	19.3	32.5
3.23	1.75	2.4	15.10	13.1	25.4	26.9	21.3	..
3.70	2.2	3.1	15.25	12.7	..	27.05	..	32.8
5.00	2 4	2 8	16.5	13.2	25.3	29.7	21.9	..
5.80	2 5	3.0	17.5	13.1	..	30.6	22.8	34.2
7.05	3.3	3.75	18.65	14.5	24.9	34.35	23.7	..
805	4.15	6.9	18.8	14.4	..	35.3	..	37.8
9 30	5 3	8.3	20.7	..	25 1	37.5	23.5	40.8
10.25	6.75	11.25	20.7	..	25 4	41.5	29.6	45.0
11.2	..	188	21.6	..	25 5	42.15	..	50.7
120	10.15	23.1	21.4	165	257	44.4	27.0	52.3
13 3	12 9	..	232	182	293	46.8	32.4	56.5
12.35	..	24.9						

with the fiber after it has been partially dried at the pump is not removed regularly, but that a large part is taken out in the first washing. After this, each washing removes a definite portion and in every case after the second washing the alkali is removed in small, gradually decreasing amounts. It would appear therefore that each washing diagram consists of two parts, the first indicating a rapid, and the second a much slower, removal of sodium hydroxide by the alcohoi.

After obtaining a large number of diagrams of essentially the same form (particularly of type B) which seem to show a sharp break, it was concluded that they might be interpreted by assuming that the first portion represented easily removable alkali which was not combined with, or adsorbed on the fiber, while the second portion might be considered as adsorbed, or combined alkali which is removed slowly. The discontinuity in the diagram then is presumed to mean that point where adhering liquid, and superfluous solution entering the interior of the fibers due to osmotic effects, is removed.

The meaning of the extrapolation is best made clear by considering Curve B, Fig. 1 which holds for a range of concentrations 2–34% sodium hydroxide by weight. By analogy with washings 3, 4 and 5, it appears logical to regard the second washing as made up of part derived from the alkali present in the first washing liquor and part derived from the fiber. Assuming then that washing 3, 4 and 5 represent the general trend of removal of absorbed sodium hydroxide it is to be anticipated that the second washing is made up of a proportional amount derived from the fiber and extrapolation to this point therefore was employed. The extrapolation was not continued to the first washing, since it was thought that in the presence of such a large amount of easily removed alkali, none of the firmly bound sodium hydroxide would be taken out.

A different extrapolation was employed for very concentrated alkali solutions (34–47% by weight), A, Fig. 2. More washings are required to remove a more concentrated adhering solution, which, with the correspondingly higher viscosity, must be intrinsically greater in amount. From the curves the break was indicated at the third washing and therefore extrapolation to this point was carried out. Further, in the use of very dilute solutions (0–2%) it is apparent that the first washing might remove alkali from the interior of the fiber itself and this was also indicated by the graph, C, Fig. 2. Accordingly extrapolation was carried to the first washing.

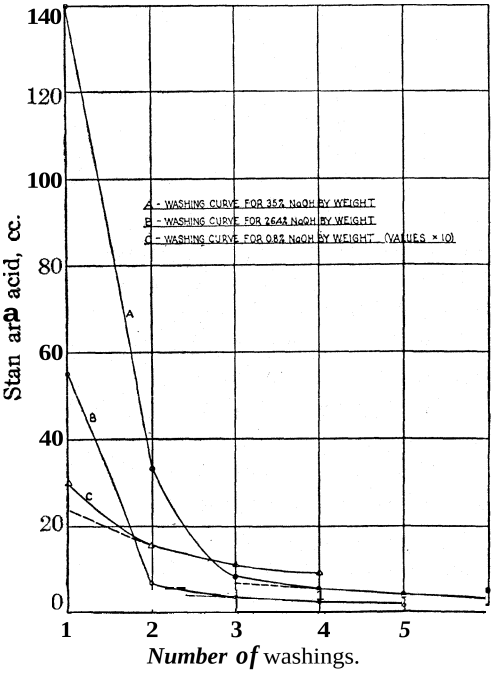

Fig. 2.

It is to be noted that the washing period is short. This has been so made purposely in order to accentuate the point at which the direction of the curve changes. It may be pointed out, however, that a ten-minute washing interval led to the same absorption value within 1%.

According to a recent paper by Neale,[29] swelling in the case of cellophane is due to osmotic effects arising from a Donnan Membrane Equilibrium; if this is indeed the case, alcohol would in all probability upset this so far as the "osmotically transferred" alkali and water are concerned, but it does not necessarily follow that the combined or adsorbed alkali is appreciably affected.

Interpretation of the Absorption Curve.—Curve I, Fig. 3, shows the relation between the amount of caustic alkali associated with the fiber and the concentration of the solution producing the absorption. The most significant feature of the curve is the almost vertical portion showing a discontinuity at a concentration of 12.5 g. of sodium hydroxide per 100 g. of solution,[30] and continuing horizontal to the concentration axis until a

[29] S. M. Neale, J. Text. Inst., 20, T373 (1929).

[30] While the authors realize that from the standpoint of the phase rule, final, i. e.,

concentration of 21.5 g. of sodium hydroxide per 100 g. of solution is reached.

The break occurs where the mole ratio of sodium hydroxide to cellulose is 1:1, *viz.*, a concentration of alkali in the solid phase of 25.3 g. of sodium hydroxide per 100 g. of cellulose as compared to a theoretical value of 24.7% for a compound of the type $(C_6H_{10}O_5)\cdot NaOH$.

This is in harmony with the formation of a compound of that composition when interpreted on the basis of the phase rule. If the system in question were merely cellulose–soda cellulose–sodium hydroxide, then the approximately vertical portion of the curve would indeed be perpendicular. A classic example of this is given by Appleyard and Walker[31] for the system diphenylamine–picric acid–diphenylamine picrate.

In the case under review, however, it is believed that superimposed adsorption causes the deviation of the almost upright portion from the vertical. This point of view is substantiated by Biltz,[32] who used Fe_2O_3–sodium alizarate and Fe_2O_3–sodium arsenite. That part of the curve horizontal to the concentration axis simply indicates that only a 1:1 compound exists and that there is no superimposed adsorption until a concentration of 21.5% is reached.

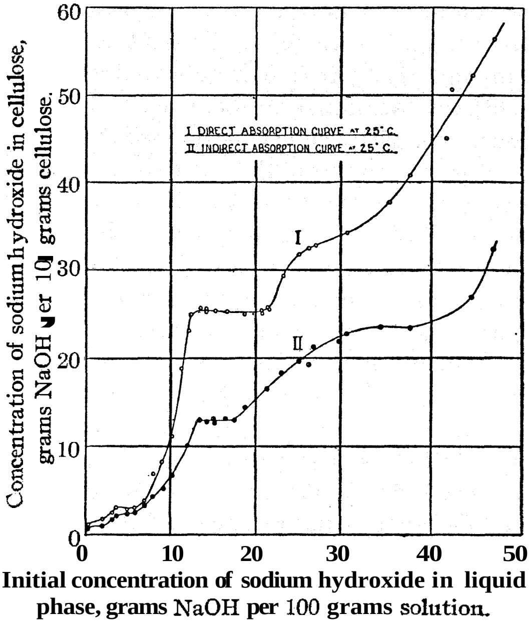

Fig. 3.

The discontinuity, therefore, is in harmony with the concept of the formation of some compound between cellulose and sodium hydroxide in equal stoichiometric proportions, within the limit of experimental error, which is estimated as about 3% for this section of the curve.

Significantly enough the discontinuity in Curve II, Fig. 3, which represents the results of the indirect method of measurement, starts at almost the

equilibrium, concentrations should have been plotted, the change in concentration of the solutions employed is so small as to render any effect in changing the shape of Pig. 2 negligible.

[31] J. R. Appleyard and J. Walker, *J. Chem. Soc.*, 69, 1334 (1896).

[32] W. Biltz, *Ber.*, 38, 4143 (1905).

same concentration of alkali, and it would seem that this too indicates compound formation, as Vieweg stated, although the composition, neglecting the effect of water absorption, is given by him as $2(C_6H_{10}O_5)\cdot NaOH$.

Further inspection of Curve I reveals also the possibility of the existence of a compound between the concentrations of 4 to 6% alkali by weight, and also on Curve II between these limits. Rumbold[26] also found a similar halt in his titration curve in this region. If such a compound does exist, the composition would be $(C_6H_{10}O_5)_8\cdot NaOH$, corresponding to the observed value of 3%, theory demanding 3.07% alkali in the cellulose.

The second break in Curve II, Fig. 3, at the higher concentrations has no analog in Curve I and the evidence for a second compound as proposed by Vieweg[7] is therefore discounted. A 1:1 compound between cellulose and sodium hydroxide is indicated within the limits of experimental error, which is estimated at about 3%. The idea of compound formation is in harmony with the chemical evidence.

Karrer[24] supports this view by a consideration of the analogous cases of other polyhydric alcohols. He points out that it is a general property of the alcohols to form compounds with alkalies, not only of the simple alcoholate type but in the case of polyhydric alcohols, compounds of a complex nature, as for example the compounds between glycerol and alkali, alkaline earth and heavy metal hydroxides.

Blanco[18] states that the phenomenon of the esterification of alkali cellulose with carbon disulfide, or benzoyl chloride, supports the idea that alkali cellulose has alcoholate properties. Herzog[33] has shown that the absorption bands in the infra-red region of the spectrum of cellulose and mercerized cellulose are distinctly different. The conception that alkali cellulose is a definite compound is further substantiated to some extent by x-ray analysis.

Taking the hydroxides of lithium, sodium and potassium, Katz[34] showed that abnormalities in the x-ray diagram coincide with the first break in the "Vieweg curve," the cellulose spectrum disappearing and new lines being formed by the absorption of nearly equimolecular amounts of these alkalies.

Whether the compound formed, and showing the new spectrum, is alkali-cellulose or an isomer of cellulose is, in his opinion, undecided.[35] The original lines disappear at 10.6% LiOH, 16% NaOH and 24% KOH, which are the concentrations at which the formation of alkali celluloses is most marked.

The difference observed between Curves I and II is due essentially to the fact that cellulose has absorbed water as well as alkali, and therefore the results as determined indirectly will be too low.

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[33] R. O. Herzog, *Z. physik. Chem.*, 121, 136 (1926).

[34] J. R. Katz, *Cellulosechemie*, **6**, 35 (1925).

[35] J. R. Katz, *Z. Elektrochem.*, 31, 157 (1925).

The Absorption of Water.—It is a simple matter to calculate the water taken up by the fiber,

Let m = mass of cellulose
v = volume of original sodium hydroxide solution of density d
b = number of grams of sodium hydroxide in this solution
x = amount of alkali absorbed, or combined with m grams of cellulose as directly determined
y = mass of water absorbed in grams
c = final concentration in grams of sodium hydroxide per 100 grams of solution

Then weight of alkali in solution at equilibrium = $b - x$ and total weight of solution = $vd - x - y$

$$\frac{c}{100} = \frac{b - x}{vd - x - y}$$

x having been determined, y is readily calculated since all the other factors are known.

$$\text{Then \% water absorbed} = \frac{100y}{m}$$

The results of this calculation are contained in Table II and are plotted in Fig. 4. *The curve is remarkable from the point of view that the maximum absorption of water takes place at about 14% alkali concentration by weight, which is the point of maximum swelling as determined by Collins and Williams.*[36] In general maximum swelling is taken as the point where total maximum absorption occurs.

TABLE II

RESULTS OF CALCULATIONS

Init concn. of NaOH in g./100 g. of soln.	Final concn.	Water absorbed, g./H_2O/100 g. of cellulose	Init concn. of NaOH in g./100 g. of soln.	Final concn.	Water absorbed, g./H_2O/100 g. of cellulose	Init. concn. of NaOH in g./100 g. of soln.	Final concn.	Water absorbed, g /H_2O/100 g. of cellulose
0.32	0.28	122	10.25	9.90	78 7	23.2	22 50	30 8
2.05	2.00	83.9	12.00	11.50	97.5	25.1	24 2	36 7
3.23	3.10	62.8	13.4	12.75	92.8	2625	25 5	42 3
3.70	3.55	44.9	14.15	13.80	113	30.6	29 7	19 7
5.00	4.90	31.3	15.1	14.55	66.8	27.5	36 8	30 0
5.80	5.60	10.2	16.5	15.70	50.3	41.5	41 0	36 7
7.05	6.85	1.3	18.65	17.95	44.0	44.4	43 3	24 7
8.05	7.65	15.2	21.4	20.70	23.0	468	46 4	43 6
9.30	9.05	24.7						

Quantitative Analysis of the **"Soda Cellulose."**[37]—A series of quantitative experiments to determine whether the compound was in reality a

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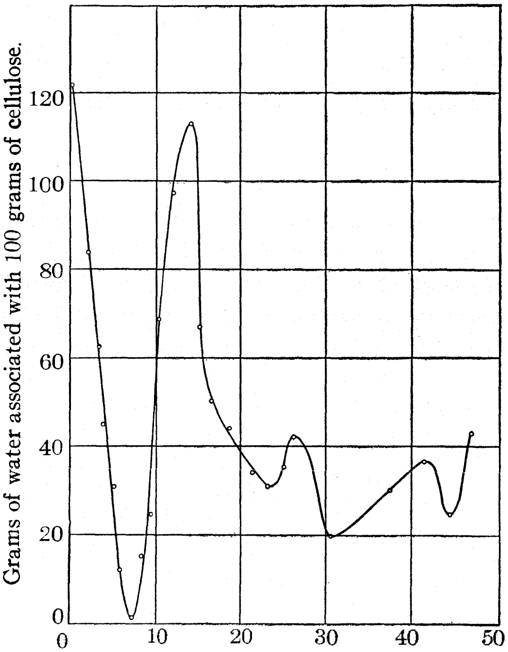
[36] G. E. Collins and A. M. Williams, *J. Text. Inst.*, *14*, T287 (1923).

[37] After the completion of this manuscript, there appeared the interesting communication of Rassow and Wolf [*Ber.*, 62, 2949 (1929)]. These authors from the results of their analysis of a soda cellulose obtained by washing with absolute alcohol to neutrality, using alizarin yellow as indicator, claim to have obtained a definite compound of the formula $C_{12}H_{20}O_{10}\cdot NaOH$. The present authors, however, see no reason either for the arbitrary choice of this indicator, or the lengthy washing period employed, which must in their experience remove far more sodium hydroxide than is present in the adhering surface layer, *i. e.*, the uncombined material.

cellulosate, or a loose addition compound, was initiated. Following the same technique by which the values in Curve I, Fig. 2, were obtained, cotton was immersed in solutions of alkali having concentrations ranging between **13** and 20% by weight. Since as indicated on the curve (Fig. 1), the surface layer of alkali is practically entirely removed by one washing, the product was therefore submitted to a simple washing prior to analysis.



Initial concentration of sodium hydroxide in liquid phase, grams of NaOH per 100 grams of solution.

Fig. 4.

Analyses were carried out in the following way. The alkali-cellulose having been dried at 70° for six hours to constant weight in a vacuum over phosphoric anhydride and calcium chloride, was rapidly transferred to a stoppered weighing bottle, weighed and the alkali present determined directly by titration. Direct determinations of sodium as sulfate were carried out in a platinum crucible, but since the results were identical with those found by titration, this latter method was generally used because of its simplicity.

Carbon and hydrogen were found thus: the dried "soda cellulose" was placed in a platinum boat, the weight of which, when contained in a stoppered bottle, was known. The boat was heated at 78° for six hours in a vacuum in the presence of phosphoric oxide to constant weight, quickly transferred to the weighing bottle, weighed and then subjected to a macro combustion in oxygen in the usual way. Assuming that the sodium hydroxide quantitatively removed carbon dioxide to form carbonate, a correction was applied to find the percentage of carbon. This assumption has previously been used with success in the combustion of complex cobalt oxyoxalates and malonates when potassium

TABLE III

ANALYTICAL RESULTS

NaOH, **initial concn. in** g./100 **g. of solution.**	13.5	15.5	17.0	18.3	19.65
Na	12.40	12.35	13.10	13.31	13.51
C	37.2	36.9	36.2	36.5	35.6
H	4.9	5.1	5.0	5.0	5.0

and alkaline earth metals were present (Percival and Wardlaw).[38] The results are given in Table III.

Is the Product a "Cellulosate" or an "Addition Compound"?—The attempt was made to decide whether the 1:1 compound is an addition compound or an alcoholate. The analytical figures which would be obtained for each are given below.

		Na	C	H
$C_6H_9O_5Na$	(Calcd.)	12.50	39.13	4.89
$C_6H_{10}O_5 \cdot NaOH$	(Calcd.)	11.36	35.64	5.44

From the results of the experiments portrayed in Graph I, Fig. 2, it was concluded that the mean probable error between concentrations of alkali of 13 and 20%, if the first washing value had been taken instead of extrapolating back to that point, was 6%. Thus it would be expected that the value for sodium obtained on analysis, if only one washing were carried out, would he high and the other percentages correspondingly low. The mean values from Table III are Na, 12.03; C, 36.5; H, 5.0. Applying the mean value for the correction, namely, 6%, these percentages become: Na 12.16; C, 36.9; H, 5.07.

The fact that the corrected values occupy an intermediate position between those demanded by theory for the two formulas, allows the assumption to be made that a mixture of the two forms may be present, *viz.*, $(C_6H_9O_5Na)_x$ and $(C_6H_{10}O_5 \cdot NaOH)_x$. The tentative suggestion is now put forward that an equilibrium of the following type may exist

$$(C_6H_{10}O_5 \cdot NaOH)_x \leftrightarrows (C_6H_9O_5 \cdot Na)_x + xH_2O$$

The present method involves subjecting the cellulose to the action of an alkaline solution and a "direct" determination of the amount of absorbed alkali by a standard washing procedure. In previous investigations the washing has been carried out by a variety of methods, involving in general the use of one or other indicator in alcoholic solution, a procedure criticized by many workers due to "end-point" difficulties and the arbitrariness of the method.

By replacing the use of an inductive, and employing a graphical, statistical method of extrapolation, it has been found possible, as indicated above, to determine accurately the amount of sodium held in chemical union.

The results establish the fact that "soda cellulose" is formed from the interaction of one mole of sodium hydroxide with 1 (not 2) anhydroglucose units. At the present time it is not possible to state definitely either the structure of the addition compound first formed, or the type of cellulosate into which it apparently changes, although the changes may possibly take place as shown below

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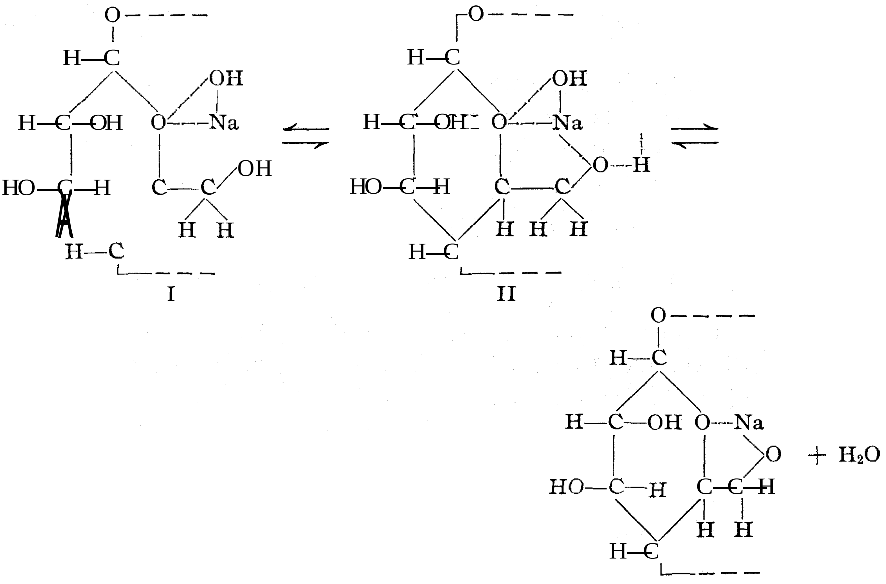
[38] E. G. V. Percival and W. Wardlaw, *J. Chem. Soc.*, 2628 (1929).



I II III

In this scheme it is assumed that the sodium hydroxide first attaches itself to the oxygen atom. In the second phase, the sodium, through the exercise of subsidiary valency forces, attaches itself also to the oxygen atom of the primary alcohol group. This compound may then be assumed to lose a molecule of water, yielding the product III, which is the substance from which cellulose xanthogenate is formed.

It is also considered likely that "coordination compounds" of this type may be formed from the sodium hydroxide addition compound involving an anhydroglucose unit of one "cellobiose chain" and the primary alcohol group of a second one. Such an assumption may possibly have some bearing on the nature of "swelling" and hydration resulting from the effect of alkalies on cellulose.

Summary

1. The absorption of sodium hydroxide by cellulose has been studied over a wide range of concentrations at 25° by a carefully controlled method of washing, thus avoiding the inaccuracies associated with the use of indicators.

2. Evidence of chemical compound formation between alkali concentrations of 12.5 and 21.5% by weight is found.

3. *The compound may be regarded as resulting from the interaction of one molecule of sodium hydroxide with each anhydroglucose unit of the cellulose.* There would seem to be no definite proof of the existence of the compound $(C_6H_{10}O_5)_2 \cdot NaOH$ as the main product formed.

4. The absorption of water by cellulose during the action of the alkali

solutions was studied, being calculated from a knowledge of the "direct" and "indirect" figures.

5. Maximum absorption of water is shown to occur at a concentration of alkali of about 14% by weight at 25°, *which corresponds with that concentration at which maximum swelling has been observed by other workers.*

6. Direct quantitative analysis of a soda cellulose which has been washed once with alcohol leads to the assumption that the product formed may be the result of an equilibrium reaction of the nature of $(C_6H_{10}O_5\cdot NaOH)_x \rightleftarrows (C_6H_9O_5Na)_x + xH_2O$. The nature of the structure of each of these compounds is uncertain but possibly in each case inter-micellary and residual-valence forces are involved.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

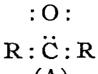
THE CLEAVAGE OF CARBONYL COMPOUNDS BY ALKALIES. I. TRIHALOMETHYL KETONES OF THE MESITYLENE SERIES

BY REYNOLD C. FUSON AND JOSEPH T. WALKER

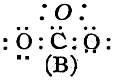
RECEIVED APRIL 7, 1930 PUBLISHED AUGUST 5, 1930

The large number of carbonyl compounds which undergo cleavage of the carbon chain when treated with alkalies suggests a cleavage mechanism arising from some property inherent in the carbonyl group. If we consider the cleavage of β-diketones, β-keto acids, nitromethyl, cyanomethyl and trihalomethyl ketones, for example, it is apparent that the carbonyl group is the structural element characteristic of the type. It is true also that the carbon atom which separates from the carbonyl carbon atom in the cleavage bears in each case one or more so-called negative groups, but the wide variety of these which are effective shows that this influence is of a very general nature. It seemed probable, therefore, that the explanation of this type of chain cleavage would be found in the properties of the carbonyl group. The purpose of the present paper is to present a theory developed on this basis.

It is assumed, in the first place, that in the *active form* of the carbonyl group the oxygen atom is singly bound to the carbon atom. The latter has, therefore, only six electrons in its valence shell **(A).** This idea has been used by Carothers[1] and by Latimer and Porter.[2] Latimer and Rodebush[3] have called attention to the fact that the carbon atom in solid carbonates probably has only six electrons in its shell (B). As Carothers has pointed out, this picture of the carbonyl group furnishes a satisfactory basis for the interpretation of addition reactions. The carbonyl carbon has **a** tendency to complete its octet of electrons by coordinating with an



(A)



(B)

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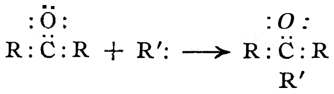
[1] Carothers, THIS JOURNAL, 46, 2226 (1924).

[2] Latimer and Porter, *ibid.*, 52, 206 (1930).

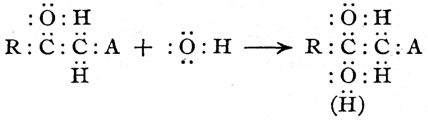
[3] Latimer and Rodebush, *ibid.*, 42, 1419 (1920).

atom which has an unshared pair of electrons. Thus the reaction with the Grignard reagent would consist in the coordination of the carbonyl carbon atom with the alkide ion of the Grignard reagent



$$\begin{array}{c}:\ddot{O}:\\ R:\ddot{C}:R\end{array} + R': \longrightarrow \begin{array}{c}:O:\\ R:\ddot{C}:R\\ R'\end{array}$$

If it is now assumed that the carbonyl carbon will tend to coordinate in a similar way with hydroxyl ion, we arrive at the following results

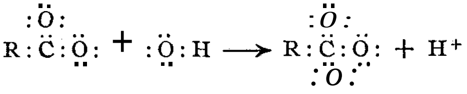


$$\begin{array}{l}:\ddot{O}:H\\ R:\ddot{C}:\ddot{C}:A\\ \quad\;\;\ddot{H}\end{array} + :\underset{..}{\ddot{O}}:H \longrightarrow \begin{array}{l}:\ddot{O}:H\\ R:\ddot{C}:\ddot{C}:A\\ :\ddot{O}:\ddot{H}\\ \;\;(\ddot{H})\end{array} \qquad (1)$$

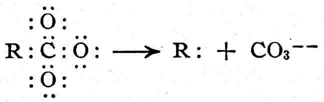
This tendency of ketones to take up hydroxyl is, moreover, well known. It is also known that the tendency is enhanced by the presence of a "negative" group, A, on the adjacent carbon atom. An example of this is the hydration of chloral. It will be noted that the deficiency of the carbonyl carbon atom will increase with increase in the residual atomic charge on the a-carbon atom. In other words, the tendency of the carbonyl carbon atom to complete its octet by coordination will increase as the negative nature of A is increased.

It is postulated that when the carbonyl carbon atom has united with an oxygen atom its hold on the pair of electrons joining it to the a-carbon atom will be decreased, enabling the latter in certain cases to separate as an ion. The tendency for this carbon atom to separate in this manner will be favored by negative groups which it may hold.

The argument may be illustrated by the case of the decarboxylation of acids by heating with alkalies. The foregoing theory leads to the following steps



$$\begin{array}{l}\;:\ddot{O}:\\ R:\ddot{C}:\underset{..}{\ddot{O}}:\end{array} + :\underset{..}{\ddot{O}}:H \longrightarrow \begin{array}{l}\;:\ddot{O}:\\ R:\ddot{C}:\ddot{O}:\\ \;:\ddot{O}:\end{array} + H^+ \qquad (2)$$

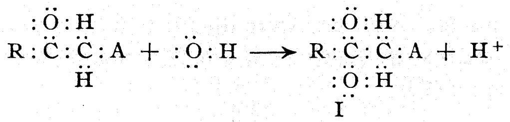


$$\begin{array}{l}\;:\ddot{O}:\\ R:\ddot{C}:\ddot{O}:\\ \;:\underset{..}{\ddot{O}}:\end{array} \longrightarrow R: + CO_3^{--} \qquad (3)$$

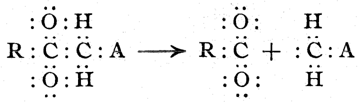
$$R: + H^+ \longrightarrow R:H \qquad (4)$$

Equation 2 shows the coordination of the carbonyl atom in the acylate ion with hydroxyl (the latter would probably lose its proton in the process). When it is remembered that the carbonate ion is very stable, the ionization shown in Equation 3 seems to follow as a consequence of Equation 2.

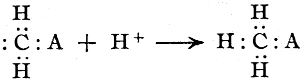
Returning now to the case of ketones, it is apparent that, formally at least, the possibilities are the same as those presented by the case of the carboxyl group.



$$\begin{array}{c}:\ddot{\mathrm{O}}:\mathrm{H}\\ \mathrm{R}:\ddot{\mathrm{C}}:\ddot{\mathrm{C}}:\mathrm{A}\\ \ddot{\mathrm{H}}\end{array} + :\ddot{\mathrm{O}}:\mathrm{H} \longrightarrow \begin{array}{c}:\ddot{\mathrm{O}}:\mathrm{H}\\ \mathrm{R}:\ddot{\mathrm{C}}:\ddot{\mathrm{C}}:\mathrm{A}\\ :\ddot{\mathrm{O}}:\mathrm{H}\\ \mathrm{I}\end{array} + \mathrm{H}^+ \qquad (5)$$



$$\begin{array}{c}:\ddot{\mathrm{O}}:\mathrm{H}\\ \mathrm{R}:\ddot{\mathrm{C}}:\ddot{\mathrm{C}}:\mathrm{A}\\ :\ddot{\mathrm{O}}:\mathrm{H}\end{array} \longrightarrow \begin{array}{c}:\ddot{\mathrm{O}}:\\ \mathrm{R}:\ddot{\mathrm{C}}\\ :\ddot{\mathrm{O}}:\end{array} + \begin{array}{c}\mathrm{H}\\ :\ddot{\mathrm{C}}:\mathrm{A}\\ \ddot{\mathrm{H}}\end{array} \qquad (6)$$

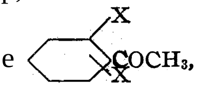


$$\begin{array}{c}\mathrm{H}\\ :\ddot{\mathrm{C}}:\mathrm{A}\\ \ddot{\mathrm{H}}\end{array} + \mathrm{H}^+ \longrightarrow \begin{array}{c}\mathrm{H}\\ \mathrm{H}:\ddot{\mathrm{C}}:\mathrm{A}\\ \ddot{\mathrm{H}}\end{array} \qquad (7)$$

In the case of ketones, the tendency to coordinate with hydroxyl and the tendency of the resulting complex (I) to break down into an acylate ion and an alkide ion will depend on the nature of **A.** The greater the residual atomic charge on A, the greater will be the tendency for coordination and likewise for subsequent cleavage by ionization. This, of course, is in agreement with the facts.

It should be pointed out that the process represented in Equation 5 is simply an electronic formulation of the commonest type of reaction of a carbonyl group, an addition. It is well known that certain ketones will not undergo these typical addition reactions. It seemed reasonable to suppose, accordingly, that these same ketones would not suffer cleavage by alkalies. This, indeed, provides a means of testing the validity of the mechanism here proposed.

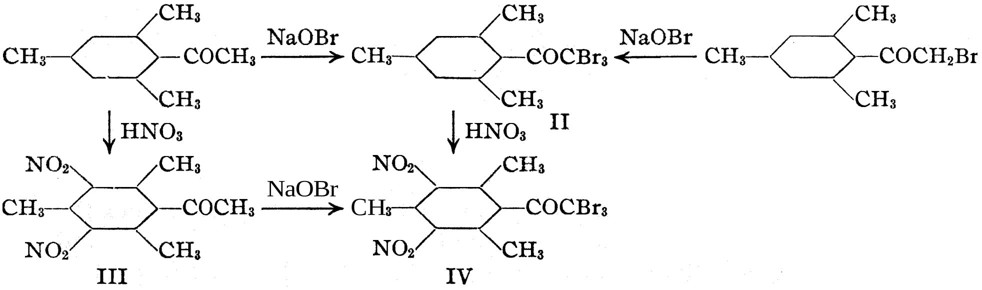
The iodoform type of reaction involving methyl ketones seemed most suitable for this study. The test of the addition theory for the cleavage may be stated as follows.

The cleavage of trihalomethyl ketones in the presence of alkalies proceeds with extreme ease. If, now, the cleavage is dependent, as postulated, on an addition reaction of the carbonyl group, it should be slowed down or inhibited in the ease of ketones of the type 

in which the carbonyl group is known to be practically inert as far as addition reactions are concerned. Experiment has supported the theory. Trihalomethyl acetophenones in which both ortho positions are filled have been prepared and have been found to be stable to alkali.

Trihalomethyl Mesityl Ketones.—The preparation of α,α,α-tribromo-2,4,6-trimethylacetophenone (II) was accomplished by the bromination of acetomesitylene by treatment with a solution of sodium hypobromite. The resulting compound melts at 68.5–69° and contains three atoms of bromine. Although the method of synthesis left little doubt as to the position of the three atoms of bromine in the molecule, it was necessary, of course, to prove beyond any doubt that none of these was in the mesityl group.

That the two nuclear positions were unsubstituted was demonstrated by preparing the dinitro derivative, α,α,α-tribromo-2,4,6-trimethyl-3,5-dinitro-acetophenone (IV).

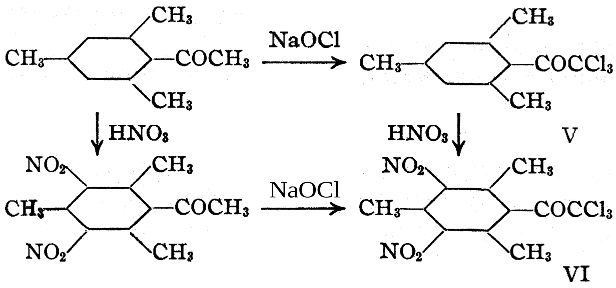


It was obtained by nitration of II. It was found possible to prepare IV in another way which, it is felt, adds to the evidence in favor of the structure written for this compound. By nitration of acetomesitylene, 3,5-dinitro-acetomesitylene (III) was obtained, and this compound when treated with a solution of sodium hypobromite gave a tribromo derivative which was shown by the method of mixed melting points to be identical with IV.

That the bromine atoms occupy the alpha positions is further supported by the fact that α-bromo-2,4,6-trimethylacetophenone when treated with a sodium hypobromite solution gave the tribromo derivative, II.

It was later found possible to demonstrate the position of the bromine atoms by a decomposition method. Although attempts at hydrolysis of the tribromo compound gave only oils which could not be identified, treatment with silver nitrate yielded β-isodurylic acid. Although the mechanism involved in this decomposition is not clear, the result shows beyond question that the three bromine atoms of the tribromo compound are in the acetyl side chain.

By use of the methods just described for the tribromo ketones, the corresponding trichloro ketones have been prepared. The series offers a close parallel to that of the bromine derivatives. α,α,α-Trichloro-2,4,6-trimethylacetophenone (V) was obtained by treating acetomesitylene with a solution of sodium hypochlorite. This compound was an oil which gave

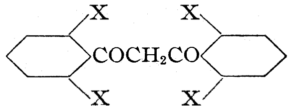


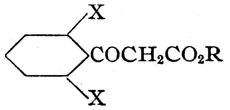
a dinitro derivative, α,α,α-trichloro-2,4,6-trimethyl-3,5-dinitro-acetophenone (VI), melting at 100.1–100.6°. Compound VI was obtained also by treating 2,4,6-methyl-3,5-dinitro-acetophenone with a solution of sodium hypochlorite. The two samples prepared in the two ways indicated were shown to be identical by the method of mixed melting points.

Returning to the point in question, the stability of trihalomethylmesityl ketones toward alkalies, it is believed that the above methods of synthesis of II, IV, V and VI not only show these compounds to be of the desired type but also that they are, indeed, stable to alkali. Experiments showed, in fact, that these compounds could be prepared in 40% solutions of sodium hydroxide. There can, therefore, be no question as to their stability toward this reagent.

The cleavage theory here presented carries with it certain implications which must be recognized. It follows, for example, that compounds of the types VII and VIII

VII





VIII

will not readily undergo the "acid" cleavage on treatment with alkali. This prediction is borne out by the work of Behal and Anger,[4] who found that di-isoduryloylmethane, a compound of type VII, could be cleaved only by heating with concentrated alkali in a sealed tube at 300°.

Experimental Part

α,α,α-Tribromo-2,4,6-trimethylacetophenone (II).—A dilute solution of sodium hypobromite was prepared by slowly adding 150 g. of bromine to an ice-cold solution of 150 g. of sodium hydroxide in 1500 cc. of water. To this solution in a 3-liter flask equipped with a stirrer was added 16 g. (0.1 mole) of acetomesitylene. The reaction mixture was stirred at room temperature for a period of two days, at the end of which time a colorless crystalline substance was obtained. This, when filtered and recrystallized from alcohol, separated as thick colorless needles melting at 68.5–69°. The yield was 35.5 g. or 89% of the theoretical.

Anal. Calcd. for $C_{11}H_{11}OBr_3$: Br, 60.1. Found: Br, 59.9.

α,α,α-Tribromo-2,4,6-trimethyl-3,5-dinitro-acetophenone (IV).—Five grams of the tribromo-acetomesitylene was dissolved in 25 cc. of ice-cold fuming nitric acid (sp. gr. 1.60). The solution was then poured slowly with stirring into 200 cc. of ice water, and the precipitate allowed to crystallize. This material was filtered and recrystallized from alcohol. It separated in the form of long, slender needles melting at 114.6–115.1° (corr.); yield, 4.9 g. or 80% of the theoretical.

Anal. Calcd. for $C_{11}H_9O_5N_2Br_3$: Br, 49 0. Found: Br, 48.8.

3,5-Dinitro-acetomesitylene (III).—Five grams of acetomesitylene was poured slowly with stirring into 50 cc. of ice-cold fuming nitric acid. The solution was then poured slowly into 200 cc. of ice water. The colorless precipitate was filtered and the dinitro-acetomesitylene extracted from a small amount of insoluble material with al-

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[4] Behal and Anger, Bull. soc. chim., [3] 9, 702 (1893).

cohol. The solution upon cooling deposited colorless crystals melting at 139.6–140.6° (corr.); yield, 4.5 g. or 58% of the theoretical.

Anal. Calcd. for $C_{11}H_{12}N_2O_5$: C, 52 3; H, 4 8. Found: C, 52.3; H, 4.8.

α,α,α - Tribromo - 2,4,6 - trimethyl - 3,5 - dinitro - acetophenone (IV). (Second Method.)—Two grams of dinitro-acetomesitylene was placed in a 150-cc. flask with 150 cc. of dilute sodium hypobromite solution prepared as described above. The reaction mixture was shaken occasionally during a period of two weeks, and was finally heated for about an hour on a steam-bath. After cooling, the precipitate was filtered and extracted twice with small portions of hot alcohol. Upon cooling the alcohol solution deposited colorless crystals melting at 114"; yield, 1.8 g. or 64% of the theoretical. A mixture of these crystals with a sample of α,α,α-tribromo-2,4,6-trimethyl-3,5-dinitro-acetophenone (prepared by the first method) showed no lowering of the melting point.

α,α,α,-Tribromo-2,4,6-trimethylacetophenone (II). (Second Method.)—Two grams of finely powdered α-bromo-2,4,6-trimethylacetophenone was added to 150 cc. of sodium hypobromite solution, prepared in the manner previously described. The mixture was allowed to stand with occasional shaking for about a week, after which time it was heated on a steam-bath, cooled and the precipitate filtered. The solid material after recrystallization from alcohol melted at 68.5–69°; yield, 1.5 g. A mixture of the crystals with a sample of α,α,α-tribromo-2,4,6-trimethylacetophenone (prepared by the first method) showed no depression of the melting point.

β-Isodurylic Acid from the Decomposition of α,α,α-Tribromo-acetomesitylene.—Five g. of α,α,α-tribromo-acetomesitylene and 7 g. of silver nitrate were placed in a 400-cc. flask equipped with a reflux condenser. To this mixture was added 150 cc. of alcohol. The resulting mixture was heated under reflux for two days. Seventy-five cc. of 10% aqueous sodium hydroxide solution was then added and the heating was continued for two hours. The silver chloride and silver oxide were removed by filtration and the alcohol by distillation. The resulting aqueous solution when acidified with dilute sulfuric acid gave an oil which soon crystallized. The compound after two recrystallizations from benzene melted at 147–149 5". A mixture of this compound with a known specimen of β-isodurylic acid (m. p. 140–151 5°) melted at 149–151°. The yield of β-isodurylic acid obtained was very small.

α,α,α-Trichloro-2,4,6-trimethylacetophenone (V).—A dilute solution of sodium hypochlorite was prepared by passing chlorine slowly into an ice-cold solution of 150 g. of sodium hydroxide in 1500 cc. of water. To th's solution in a 2-liter flask was added 16.1 g. (0.1 mole) of acetomesitylene, the resulting mixture was stirred continuously for three days at room temperature. The heavy oil which was formed was extracted with ether, dried and distilled under reduced pressure. A yield of 22 5 g, or 88% of the theoretical, was obtained. The trichloro ketone boiled at 130–140" at 5 mm.

Anal Calcd for $C_{11}H_{11}OCl_3$: Cl, 40 1. Found: Cl, 39 8.

α,α,α-Trichloro-2,4,6-trimethyl-3,5-dinitro-acetophenone (VI).—One gram of α,α,-α-trichloro-2,4,6-trimethylacetophenone (V), prepared in the manner just described, was dropped slowly into 15 cc. of ice-cold fuming nitric acid (sp. gr. 1.60), the mixture being stirred continuously. After being allowed to stand for a short time in the cold, the solution was poured into a large amount of ice water and the precipitate was allowed to crystallize. The solid was filtered and recrystallized from alcohol. It separated in long, colorless needles melting at 100.1–100.6" (corr.); yield, 1.2 g. or 89% of the theoretical.

Anal. **Calcd.** for $C_{11}H_9O_5N_2Cl_3$: Cl, 29.9. Found: Cl, 23.9.

α,α,α, - Trichloro - 2,4,6 - trimethyl - 3,5 - **dinitro** - acetophenone (VI). (Second Method.)—Two g. of dinitro-acetomesitylene was placed in a 300-cc. flask with 150 cc.

of sodium hypochlorite, prepared as described above. The reaction mixture was shaken occasionally during a period of two weeks, and was finally heated for about an hour on a steam-bath. After cooling, the precipitate was filtered and recrystallized from alcohol. It separated in long needles which proved to be identical with those prepared by the other method. The yield was 2 g. or 70% of the theoretical. A mixture of these crystals with a sample of α,α,α-trichloro-2,4,6-trimethyl-3,5-dinitro-acetophenone (prepared by the first method) showed no lowering of the melting point.

Summary

1. The cleavage of the carbon chain of carbonyl compounds under the influence of alkali is ascribed to the coordination of the carbonyl carbon atom with hydroxyl. It is assumed that the polarity of the bond between the carbonyl carbon atom and the α-carbon atom is thus enhanced. In case the substituents on the a-carbon atom are sufficiently "negative" dissociation occurs.

2. It is pointed out that, according to this theory, certain trihalomethyl ketones whose carbonyl groups do not undergo addition reactions should be stable to alkali.

3. Several such trihalomethyl ketones have been prepared and found to be unaffected by alkali.

4. These results strongly support the assumption that chain cleavage of this type is dependent on an *addition* reaction of the carbonyl group. That this is the addition of hydroxyl, as postulated by the theory here developed, seems probable.

URBANA, ILLINOIS

[FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

THE ESTIMATION OF SULFUR IN ORGANIC COMPOUNDS[1]

BY H. ZAHND AND H. T. CLARKE

RECEIVED APRIL 10, 1930 PUBLISHED AUGUST 5, 1930

In 1923 Hoffman and Gortner[2] drew attention to the applicability to organic compounds of the method for estimating sulfur in biological material devised by Benedict[3] and modified by Denis.[4] This procedure which, in the hands of the biological chemist, has practically superseded the methods of Carius and of alkaline fusion, tends to give rise to mild explosions under conditions which cannot always be controlled. In the method described below this disadvantage is almost entirely eliminated by observing suitable precautions.

The process consists in the oxidation of organic matter by means of

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[1] This work was aided by the Research Grant from the Chemical Foundation to the Department of Biological Chemistry.

[2] Hoffman and Gortner, THIS JOURNAL, 45, 1033 (1923).

[3] Benedict, J. *Biol.* Chem., 6, 363 (1909).

[4] Denis, *ibid.*, 8, 401 (1910).

nitric acid in the presence of potassium nitrate, followed by evaporation of the nitric acid and fusion of the residue, whereby organic sulfonates are converted into sulfate. The reaction is carried out in an open vessel capable of withstanding the action of the fused nitrate. The latter is decomposed by warming with hydrochloric acid and after again evaporating to dryness the residue is dissolved and treated with barium chloride.

The method, which has proved well adapted to micro-analysis, is applicable to all types of substance except volatile sulfones or compounds (such as alkyl sulfides) capable of yielding them. This limitation applies also to the Benedict–Denis method, and it may be noted that while sulfonal is reported by Hoffman and Gortner[2] as yielding no sulfate at all by the latter process, we have been able to recover 60–70% of the sulfur in sulfonal as barium sulfate. The process here described thus appears to be somewhat more vigorous.

Experimental

The reaction vessel consists of a test-tube of pyrex glass[5] or, better, clear silica. The sample is introduced, followed by an amount of pure potassium nitrate or chlorate (preferably as a 5–10% aqueous solution) equivalent to at least **30** molecular proportions for every atomic proportion of sulfur anticipated. Concentrated (65–70%) nitric acid (1cc. or more per decigram of sample) is added, and a small conical flask (or conical glass bulb) of suitable dimensions (Fig. 1) is suspended in the mouth of the reaction tube to serve as a reflux condenser. The tube is held in a clamp lined with asbestos paper at an angle of 45°, and the mixture is heated very gently over a micro-burner until the evolution of oxides of nitrogen practically ceases.

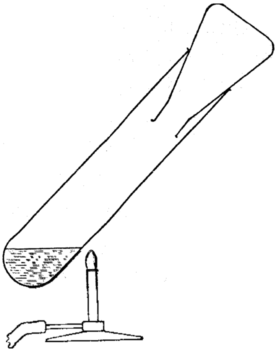

Fig 1

The burner is now shifted from a position directly under the liquid to one under the tube at a point just above the level of the liquid, and the flame is increased until it nearly reaches the wall of the vessel. The glass at this point is thus heated above the boiling temperature of the acid; a deposit of salts forms there, and in its superheated condition gradually undergoes a vigorous decomposition, while being continually subjected to the action of fresh nitric acid returning from the reflux condenser. The heating and the height of the tube above the flame are so regulated that a small proportion of the nitric acid vapor escapes without condensation. Oxalic acid and ammonium nitrate, if present, decompose and volatilize at this stage of the process. As the level of liquid in the tube falls, the tube is from time to time raised by sliding it through the jaws of the clamp. This part of the process, which occupies from one to three hours, requires a moment's attention every twenty minutes or so. During this time the vigorous secondary oxidation takes place almost completely, but by small degrees. Care must be taken not to evaporate so rapidly as to displace all of the brown oxides of nitrogen from the tube, for this may result in the removal of the bulk of the acid before oxidation is complete. In such a case the residue may deflagrate with mechanical loss of sulfate.

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[5] If a wide, heavy-walled pyrex tube be employed, it should be annealed in a glass blower's flame before use.

When all the liquid has been evaporated, the lower part of the tube is heated with an ordinary Bunsen flame, kept constantly in motion, until the residual potassium nitrate first fuses, then effervesces and finally becomes quiescent. This part of the process, which requires less than a minute, is thus carried out in an atmosphere of nitric acid vapor. The melt is allowed to cool, is treated with a small quantity (0.5–1.0 cc.) of nitric acid, and is again heated, in order to complete the oxidation of any particles which may have escaped decomposition.

After the second fusion, the cold mass is treated with 0.5–2.0 cc. of concentrated hydrochloric acid and gently heated until no more red fumes are evolved. The reflux condenser is then removed, and heating continued very gently until the residue is completely dry. The last traces of acid adhering to the walls are volatilized by warming the whole tube gently with a large flame.

The salts are then dissolved in a suitable quantity of 0.2% hydrochloric acid, the solution is filtered or centrifuged if necessary, and the sulfate precipitated in the usual way with barium chloride. In the case of micro-determinations, this precipitation may very satisfactorily be conducted in a centrifuge-tube, the barium sulfate receiving its first wash by centrifuging and decantation.

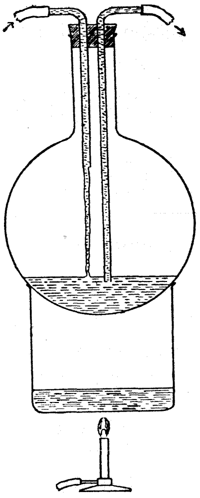

Fig 2.

When the percentage of sulfur in the substance is extremely low (as for example in cereals), so that a relatively large sample has to be taken, the preliminary oxidation may advantageously be carried out in a pyrex beaker capable of containing about six times the volume of the reaction mixture. A round-bottomed flask containing cold running water, set in the mouth of the beaker, acts as a reflux condenser (Fig. 2) The mixture is heated over a small flame to gentle boiling for fifteen to twenty hours. At the end of this time very little oxidizable organic matter remains. The mixture is transferred to the reaction tube and the decomposition is completed in the manner above described, the nitric acid rinsings being added in the final stages.

This modification of the procedure is exemplified by the estimations of total sulfur in corn starch: in one case 17.9 g. was decomposed with 50 cc. of nitric acid and 5 cc. of 5% potassium chlorate, while in another, 5.153 g. of the starch was decomposed with 25 cc. of nitric acid and 5 cc. of 5% potassium chlorate solution. In such determinations it is necessary to correct for the small amount of sulfate present in the nitric acid which, in the present instance, yielded 0.51 mg. of barium sulfate per 100 cc.

That no loss of sulfate occurs during the process is evident from a series of determinations in which varying amounts of sodium sulfate were treated as above, employing 10 cc. of nitric acid with a mixture of 0.5 g. of sodium nitrate and 0.5 g. of potassium nitrate.

S taken as Na_2SO_4, mg......	2 82	3.27	6.74	9.39	9.41	15.63	15.96	23.51
S found as $BaSO_4$, mg.......	2.81	3.30	6.91	9.31	9.53	15.75	16.18	23.61

Samples of a solution of sulfuric acid which gave 0.4465 and 0.4462 g. of barium sulfate by direct precipitation gave 0.4463 and 0.4455 g. of barium sulfate when treated as above.

An attempt was made to employ perchloric acid together with the nitric acid, but low results were obtained. It was found that when sodium sulfate is heated with boiling perchloric acid, an appreciable amount of sulfuric acid is volatilized: 2-cc. quantities of sodium sulfate solution which gave 0.1651 g. of barium sulfate by direct precipitation were treated with 2-cc. portions of 70% perchloric acid and evaporated to dryness during two hours: barium sulfate recovered, 0.1428, 0.1438, 0.1472 g.; loss, 13.5, 12.9, 10.8%.

The following results were obtained with various organic and biological products.

Compound	Wt. of sample	$BaSO_4$	Sulfur, % Found	Calcd.
o-Benzoic Sulfinide	0.1407 g.	0.1810 g.	17.63	17.51
	0.2155 g.	0.2766 g.	17.59	
Cystine (EK)	0.2997 g.	0.5926 g.	27.12	26.69
	6.000 mg.	11.802 mg.	26.97	
Cystine (recrystallized)	0.1694 g.	0.3314 g.	26.78	
	0.0983 g.	0.1918 g.	26.76	
Diphenylsulfone	0.2033 g.	0.1064 g.	7.18	14.67
S-Ethylcysteine	0.1903 g.	0.2907 g.	20.96	21.46
	0.2088 g.	0.3168 g.	20.83	
	0.1183 g.	0.1793 g.	20.79	
Thiocarbanilide (EK)	0.3176 g.	0.3241 g.	14.01	14.05
	0.2233 g.	0.2270 g.	13.93	
	0.3314 g.	0.3369 g.	13.94	
p-Toluenesulfonamide	0.1014 g.	0.1417 g.	18.54	18.73
	0.0690 g.	0.0933 g.	18.55	
Sulfonal	0.1591 g.	0.2241 g.	19.3	28.07
	2.183 mg.	2.674 mg.	16.8	
Casein ("according to Hammarsten," Sample I)	1.3530 g.	0.0757 g.	0.77	
	1.0810 g.	0.0586 g.	0.74	
	1.7622 g.	0.1000 g.	0.78	
	1.1962 g.	0.0680 g.	0.78	
	1.1297 g.	0.0632 g.	0.77	
Casein ("according to Hammarsten," Sample II)	0.4884 g.	0.0257 g.	0.722	
	0.0747 g.	3.839 mg.	0.705	
	0.0625 g.	3.240 mg.	0.712	
Corn Starch (Duryea's)	17.9 g.	25.028 mg.	0.019	
	5.153 g.	6.750 mg.	0.018	
Egg Albumin (Commercial)	0.9948 g.	0.1151 g.	1.59	
	0.9512 g.	0.1123 g.	1.62	
	0.9963 g.	0.1187 g.	1.63	
	0.8076 g.	0.0942 g.	1.60	
Wool	0.1776 g.	40.168 mg.	3.10	
	0.0489 g.	10.325 mg.	2.90	

Urine.—The total sulfur in three different samples was determined, in 10-cc. portions, employing both the method here described, and that due to Benedict and Denis. In the former, the 10 cc. of urine was heated with 10 cc. of nitric acid and 1 g. of potassium nitrate. The results are reported in milligrams of sulfur:

Sample	A	B	C
Present method	4.3	8.5	6.7
Benedict-Denis	4.3	9.1	6.9

Summary

1. Sulfur in organic combination can be estimated with reasonable accuracy as sulfate after oxidizing by fusion with potassium nitrate in presence of nitric acid.

2. The method fails in the case of volatile sulfones and compounds from which such sulfones are produced by the action of nitric acid.
3. Reproducible results can be obtained with biological material.
4. The process is adaptable to the estimation of sulfur in materials containing as little as 0.02%.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHT OF LEGUMIN

BY BERTIL SJÖGREN AND THE SVEDBERG

RECEIVED APRIL 21, 1930 PUBLISHED AUGUST 5, 1930

In recent communications from this Laboratory determinations of the molecular weights and of the P_H-stability regions of some oil seed globulins, *viz.*, edestin,[1] amandin and excelsin[2] by means of the ultracentrifugal method, have been given. These proteins as well as the three other vegetable proteins, R-Phycocyan, R-Phycoerythrin, C-Phycocyan, so far studied with the ultracentrifuge, were all found to possess a molecular weight of 208,000, which is approximately six times the weight of egg albumin. Their molecules are spherical with a radius of 3.95$\mu\mu$. The stability regions are different for the different proteins but they all show a tendency to dissociate into lower multiples of 34,500 with increasing P_H. It was thought to be of interest to study also some representative of the proteins of the *Leguminosae* family by means of the ultracentrifuge analysis. Legumin from vetch (*Vicia sativa)* was chosen. According to the investigations of Osborne[3,4] the vetch contains only one globulin, legumin and one albumin, legumelin, while the pea and the horse bean contain legumin, legumelin and one more globulin, the vicilin. Whether the legumins extracted from the various *Leguminosae* seeds are identical is not quite clear. We have not so far made any attempt to answer this question.

Preparation of Material.—Two thousand grams of vetch flour was divided in two equal portions and each of them stirred at room temperature during twenty-four hours with 4000 cc. of 10% sodium chloride solution.[5] Enough toluene to form a layer about 1 cm. thick was added. It served the double purpose of dissolving the fat and preventing bacterial growth. The bulk of the insoluble part was removed by means of a cloth filter and the rest by centrifuging. Most of the fat had been taken up by the toluene.

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[1] T. Svedberg and A. T. Stamm, THIS JOURNAL, 51,2170 (1929).

[2] T. Svedberg and B. Sjogren, *ibid.*, 52,279 (1930).

[3] T. B. Osborne and G. F. Campbell, *ibid.*, 18, 583 (1896); 20, 406, 410 (1898).

[4] T. B. Osborne, "Vegetable Proteins," Longmans, Green and Co., London, 1916.

[5] The grinding of the vetch seed was kindly done for us in an experimental mill at the laboratory of Upsala Ångkvarn.

The PH of this solution was 5.7. Saturated ammonium sulfate solution was added to 85% saturation, the precipitate was centrifuged off, suspended in water and dialyzed for twenty-four hours against water. After that time the precipitate had dissolved leaving only a small residue. The solution was filtered and then dialyzed again until the sulfate reaction was negative. This second dialysis caused a separation of the two proteins; legumin was precipitated while legumelin remained in solution.

The legumin precipitate was centrifuged off, washed repeatedly with ammonium sulfate solution of 65% saturation and dissolved in 5% sodium chloride solution. This legumin solution was precipitated with saturated ammonium sulfate solution to 65% saturation. After standing for twenty-four hours in the ice box the precipitate was centrifuged off and washed with ammonium sulfate of 65% saturation until free from legumelin. The legumin precipitate was dissolved in phosphate buffer of PH 6.5 (0.14 *M* in KH_2PO_4 and 0.06 M in Na_2HPO_4) and dialyzed against the same buffer in the ice box until the sulfate reaction was negative: volume of solution 200 cc., concentration 3.35%.

The legumelin solution remaining after precipitating the legumin by dialysis was saturated with ammonium sulfate, After standing for twenty-four hours in the ice box the legumelin precipitate was centrifuged off, washed with ammonium sulfate, dissolved in water, dialyzed against water at 5° and finally electrodialyzed. During the dialysis and the electrodialysis a considerable quantity of protein was precipitated. The ultracentrifugal study of the solution at high speed (44,000 r. p. m.) showed it to be polydisperse. There was a considerable drift in the apparent diffusion constant indicating the presence of several molecular species. The mean value of the sedimentation constant was very low, *viz.*, 1.20×10^{-13} at 20°. The corresponding mean molecular weight would be around 7500. The legumelin is therefore not a simple protein. Most probably it only represents a mixture of decomposition products. The study of it was not pursued any further.

Specific Volume and Light Absorption.—The specific volume of legumin was measured pycnometrically at 20.2°. The solution was 0.14 *M* in KH_2PO_4 and 0.06 M in Na_2HPO_4, giving a PH of 6.5. Determinations at two concentrations, 2.45 and 1.03%, agreed within experimental error and gave V = 0.743.

The light absorption was measured by means of the Judd-Lewis spectrophotometer. At PH 6.5 the solvent was 0.14 M in KH_2PO_4 and 0.06 M in Na_2HPO_4 and the legumin concentration 0.1 and 0.4% with a thickness of layer of 2.0 and 1.0 cm., respectively. At PH 12.4 the solvent was 0.011 M in KH_2PO_4, 0.001 *M* in Na_2HPO_4, 0.059 M in NaOH and 1% in NaCl and the legumin concentration 0.2% with a thickness of layer of 1.0 cm. The position of the maximum and the minimum as well as the values of the specific extinction coefficient $\epsilon/c = 1/cd \times \log I_0/I$ (where c is the concentration, d the thickness of the solution, I_0 the intensity of the light beam after passing through the solvent and I the intensity after passing through the same thickness of solution) was found to be the same at PH 6.5 and 12.4 although, as shown by the ultracentrifugal analysis, the legumin molecule is broken up into smaller units at PH 12.4. The absorption maximum was situated at $280\mu\mu$ with $\epsilon/c = 7.5$ and the minimum at $255\mu\mu$ with $\epsilon/c = 3.0$. In Fig. 1 the absorption curve is given.

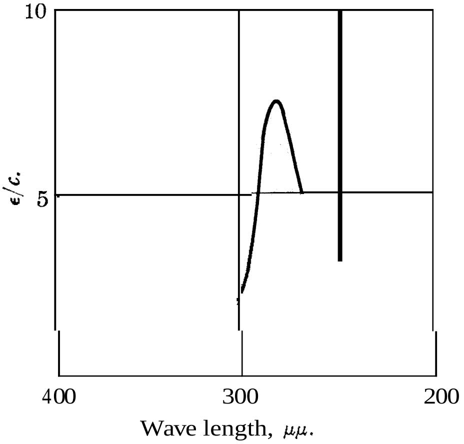

Fig. 1.

Determination of Molecular Weight.—Using the sedimentation equilibrium method the molecular weight is given by the relation

$$M = \frac{2RT \ln (c_2/c_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)}$$

where R is the gas constant, T the absolute temperature, V the partial specific volume of the solute, p the density of the solvent, ω the angular velocity and c_2 and c_1 are the concentrations at the distances x_2 and x_1 from the center of rotation.

In Table I the result of a typical run is given and in Table II are collected the data of the three equilibrium runs made on legumin.

As mean value we get 208,000 ± 5000 for the molecular weight. The fact borne out by Table I that there is no drift in the molecular weight values with distance from the center of rotation shows that legumin is homogeneous with regard to molecular weight.

TABLE I

LEGUMIN, SEDIMENTATION EQUILIBRIUM RUN

Concn., 0.11%; phosphate buffer, PH 6.8 (0.1 M in KH_2PO_4, 0.1 M in Na_2HPO_4); V = 0.743; $\rho = 1.017$; T = 293.3; length of col. of soln., 0.43 cm.; thickness of col., 0.80 cm.; dist. of outer end of soln. from axis of rotation, 5.95 cm.; speed, 5000 r. p. m. (ω = 166.7~); light absorption standard, $M/200$ in K_2CrO_4 with a thickness of layer of 0.40 cm.; source of light, mercury lamp; light filters, chlorine and bromine; aperture of objective, F:36; plates, Imperial Process; time of exposure, 30, 60 and 120 seconds; exposures made after 40, 45 and 50 hours of centrifuging.

Distances, cm.		Mean concn., %		Number of exposures	Mol. wt.
x_2	x_1	c_2	c_1		
5.87	5.82	0.084	0.073	12	213,100
5.82	5.77	.073	.064	12	203,100
5.77	5.72	.064	.056	9	215,700
5.72	5 67	.056	.049	9	212,200
5.67	5.62	.049	.043	9	194,000
				Mean	208,000

TABLE II

LEGUMIN, SUMMARY OF SEDIMENTATION EQUILIBRIUM MEASUREMENTS

Solvent KH$_2$PO$_4$, M	Na$_2$HPO$_4$, M	PH of soln.	Concn. of protein at start, %	Mean speed, r. p. m.	Mol. wt.
0.14	0.06	6.5	0.40	5600	213,000
.1	.1	6.8	.11	5000	208,000
.008	.192	8.0	.10	4800	204,000

Determination of Sedimentation **Constant.**—The high-speed oil-turbine ultracentrifuge was used for measuring the sedimentation constant $s = dx/dt \times 1/\omega^2x$ at different acidities. The temperature of the solution was between 20 and 23° during centrifuging, the time varied from two to $3^1/_2$ hours and the speed from 25,000 to 40,000 r. p. m. The determinations are summarized in Table III and Fig. 2.

TABLE III

LEGUMIN, SUMMARY OF SEDIMENTATION VELOCITY MEASUREMENTS

No.	Solvent KH$_2$PO$_4$, M	Na$_2$HPO$_4$, M	NaOH, M	NaCl, %	PH of soln.	Concn. of protein, %	$s_{20} \times 10^{13}$
1[a]	0.014	..	..	1	3.15	0.24	8.80[b]
2	.096	0.004	..	1.5	5.26	.22	11.42
3	.14	.06	..	...	6.5	1.34	11.23
4	.14	.06	..	...	6.5	0.24	11.45
5	.08	.12	..	...	6.89	.24	11.47
6	.008	.192	..	...	8.00	.22	11.89
7	.008	.032	0.018	...	8.94	.24	11.41[c]
8	.014	.037	.033	...	9.38	.25	—[c]
9	.014	.035	.035	...	10.78	.25	3.03
10	.011	.001	.059	1	12.40	.20	2.14

[a] 0.093 M in HAc. [b] Solution decomposed; 25% non-centrifugible products. [c] Mixture of approximately 44% molecules of weight 208,000 and 56% of weight 104,000.

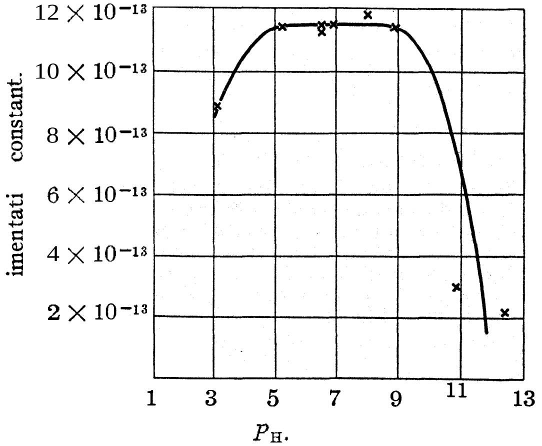

Fig. 2.

The sedimentation is independent of PH between 5 and 9. The PH range 5–9, therefore, represents the stability region of legumin. The isoelectric point[6] 5.4 is situated near the acid border of the stability region. In more acid and more alkaline solutions the legumin molecule is broken up into

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[6] F. A. Csonka, J. C. Murphy and D. B. Jones, THIS JOURNAL, 48, 763 (1926); the material used for the determination of the isoelectric point was prepared from pea.

smaller units of unequal weight. At a PH of about 9.3 molecules of half the normal weight are present. Within the stability region the sedimentation constant is 11.48×10^{-13} (mean value from the runs No. 2–7, PH 5.26–8.94). From the value 208,000 of the molecular weight and this value of the sedimentation constant the value 4.60×10^{16} for the molar frictional constant $f = [M(1 - Vp)]/s$ is obtained. The molar frictional constant for a spherical molecule is $f_0 = 6\pi\eta N(3MV/4\pi N)^{1/3}$, where η is the viscosity of the solvent. For a substance of the same molecular weight and specific volume as legumin we get $f_0 = 4.51 \times 10^{16}$. The ratio f/f_0 is 1.02 and should be unity if the legumin molecules were actually spherical. The deviation is within the limit of experimental error. The radius of the molecule, derived from the formula $r = (3MV/4\pi N)^{1/3}$, is $3.96\mu\mu$. A comparison of the values of molecular weight, sedimentation constant, frictional constant and radius for legumin with those obtained for the vegetable proteins previously studied by means of the ultracentrifugal methods[2] shows that they are identical within the limits of experimental error.

The expenses connected with these experiments have been defrayed by a grant from the foundation "Therese och Johan Anderssons Minne."

Summary

1. The molecular weight and PH-stability region of legumin have been determined by means of the ultracentrifugal methods.

2. Legumin is stable from PH 5 to 9 with a molecular weight of 208,000 ± 5000. At a PH of about 9.3 molecules of one-half the normal weight are present. At PH-values decidedly lower than 5 and higher than 9 the legumin molecule is broken up into smaller units.

3. Within the stability region the sedimentation constant of legumin is 11.48×10^{-13} and the molar frictional constant 4.60×10^{16}. The molecules are spherical with a radius of $3.96\mu\mu$.

4. The molecular weight, sedimentation constant, molar frictional constant and molecular radius of legumin are within the limits of error identical with the corresponding constants for amandin, edestin, excelsin R-phycoerythrin, R-phycocyan and C-phycocyan as previously determined by means of the ultracentrifugal methods.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE DIRECT ARSONATION OF BENZENE DERIVATIVES

BY CLIFF S. HAMILTON AND CLIFFORD G. LUDEMAN

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The methods of Bart[1] and Béchamp[2] constitute at present the only practicable means of introducing arsenic into the benzene ring. In 1921, Rosenmund[3] reported the preparation of phenylarsonic acid and *o*-carboxyphenylarsonic acid from o-bromobenzene and o-bromobenzoic acid, respectively, by treatment with tripotassium arsenite, and in 1923 Albert and Schulenberg[4] patented the preparation of mixed aromatic–aliphatic arsonic acids by replacement of nucleus-substituted halogens with sodium arsenite. This investigation was started with the idea of extending the method of Rosenmund and in this work activated aryl halides were used.

Rosenmund's synthesis of o-carboxyphenylarsonic acid was confirmed, though his directions were incomplete, and the synthesis of *p*-acetophenonearsonic acid as prepared by Albert and Schulenberg was confirmed with difficulty. In the preparation of *p*-carboxyphenylarsonic acid the yields were always quite low and hydrolysis products predominated. Low temperatures and a long reaction time produced the best yields. p-Hydroxybenzoic acid was generally isolated and phenol in increasing amounts was obtained with increased reaction temperatures.

The preparation of o-phenylenediarsonic acid from o-bromophenylarsonic acid resulted in good yields and its identity was established by the preparation of o-phenylenediarsine oxychloride according to the method of Kalb.[5] Phenol was obtained in considerable amounts as a by-product, yet boiling solutions of alkali did not convert o-bromophenylarsonic acid or *o*-phenylenediarsonic acid to phenol or other hydrolysis products.

Attempts to prepare various nitrophenylarsonic acids were unsuccessful. When o-chloronitrobenzene was used as the starting material it was always reclaimed unchanged. Using o-bromonitrobenzene, partial hydrolysis occurred at 105°, while if the reaction mixture consisting of *o*-bromonitrobenzene and an excess of 50% trisodium arsenite solution was refluxed vigorously for twenty-four hours, a small amount of an arsonated product was obtained as evidenced by the arseno-test. This was contrary to the findings of Loesner.[6] In the attempt to prepare *p*-nitrophenylarsonic acid from p-bromonitrobenzene, 45% of the calculated amount of 4,4-dibromo-

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[1] Bart, *Ann.*, 429, 55 (1922).

[2] Béchamp, Compt. *rend.*, 50, 870 (1860); *51*, 356 (1860).

[3] Rosenmund, *Ber.*, 54, 438 (1921).

[4] Albert and Schulenberg, German Patent 468,403 (1923).

[5] Kalb, *Ann.*, 423, 39 (1921).

[6] Loesner, J. *prakt. Chem.*, [2] 50, 564 (1894).

azoxybenzene was produced. Only a small amount of material was obtained which gave a positive arseno-test, but no products could be identified. In the study of 2,4-dinitrochlorobenzene the results of Balaban,[7] who reported the formation of the corresponding phenol, were confirmed rather than the production of 2,4-dinitrophenetole as published by Nijk.[8] Attempts to prepare *p*-sulfophenylarsonic acid from *p*-bromobenzene sulfonic acid were unsuccessful. The reaction was tried at various temperatures up to 160° at which point a small amount of material giving a positive arseno-test resulted.

Experimental

o-Carboxyphenylarsonic Acid (*o*-**Benzarsonic** Acid).—A mixture of 20 g. (0.1 mole) of o-bromobenzoic acid, 63 cc. of 10% potassium hydroxide solution, 20 cc. of ethyl alcohol, 40 cc. of 50% tripotassium arsenite solution and a little freshly reduced copper was refluxed at 90 to 95° for twelve hours with constant stirring. The reaction mixture was filtered hot to remove copper, made acid to congo red paper with 20 cc. of concd. hydrochloric acid and evaporated to dryness on a steam cone. The resulting residue was extracted with absolute methanol; the methanol extract was evaporated to dryness and the residue washed with ether to remove salicylic acid and unchanged o-bromobenzoic acid. The ether-washed residue was twice recrystallized from hot water after decolorization with bone black; yield, 10.1 g., 41% of the calcd. amount.

Anal. Subs , 0 2460, 0.2460: 40.00, 39.95 cc. of 0.05 *N* $KBrO_3$. Calcd. for $C_6H_4(COOH)AsO(OH)_2$: As, 30.47. Found: As, 30.47, 30.44.

Optically, o-carboxyphenylarsonic acid consists of positive biaxial crystals having a very small optic angle. The indices of refraction are $\alpha = 1.615$ and $\beta =$ a little more than 1.620 with sodium light.

***p*-Acetophenone-arsonic** Acid.—A solution of 3 g. (0.015 mole) of *p*-bromo-acetophenone in 21 cc. of 95% ethyl alcohol and a solution of 6.75 g. (0.028 mole) of tripotassium arsenite in 21 cc. of water was heated in a sealed tube at 165 to 170° for twelve hours. The contents of the tube were removed by washing with hot water and then hot alcohol, and the whole was made acid to congo red paper with 5 cc. of concd. hydrochloric acid. After cooling, the unchanged *p*-bromo-acetophenone and some precipitated arsenious oxide were removed by filtration and the filtrate was then evaporated to dryness on a steam cone. Isolation and purification of the product was carried out as outlined under o-carboxyphenylarsonic acid.

Anal. Subs., 0.2025: 33.0 cc. of 0.05 N $KBrO_3$. Calcd. for $CH_3COC_6H_4AsO(OH)_2$: As, 30.72. Found: As, 30.54.

p-Carboxyphenylarsonic Acid (p-Benzarsonic Acid).—The amounts of materials and the procedure in this preparation were the same as those used in the preparation of o-carboxyphenylarsonic acid except that *p*-bromobenzoic acid was used in place of the ortho compound and the temperature was 89 to 93° for forty-eight hours; yield, 1.14 g., 4.6% of the calcd. amount.

Anal. Subs., 0.2005, 0.20055: 32.6, 32.55 cc. of 0.05 *N* $KBrO_3$. Calcd. for $C_6H_4(COOH)AsO(OH)_2$: As, 30.47. Found: As, 30.47, 30.43.

Optically, *p*-carboxyphenylarsonic acid consists of positive biaxial crystals having a large optic angle. The crystals were incorrectly orientated for an accurate determination of the indices of refraction with the means at hand.

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[7] Balaban, J. Chem. *Soc.*, 569 (1926).

[8] Nijk, *Rec. trav. chim.*, 41,461 (1922).

o-**Phenylenediarsonic** Acid.—A solution of **14** g. **(0.05** mole) of *o*-bromophenylarsonic acid in **3.7** cc. **(0.05** mole) of **50%** potassium hydroxide and **17** cc. **(0.07** mole) of **50% trisodium** arsenite solution was refluxed at 110° for forty-eight hours. The reaction mixture was made acid to congo red paper with an excess of concd. hydrochloric acid and the solution steam distilled; the distillate yielded **0.6** g. or 14.3% of the calculated amount of phenol on extraction with ether. The phenol so obtained boiled at **180°**, gave the tribromo derivative melting at **93°** with bromine water, and gave a negative bromine test on sodium fusion. The residue from the steam distillation was cooled and filtered. The precipitate after washing with absolute methanol was dissolved in an excess of concd. ammonium hydroxide and the resulting solution treated with **7 cc.** of **30%** hydrogen peroxide; the excess of ammonia and hydrogen peroxide was removed by boiling, and the diarsonic acid obtained by reprecipitation weighed **7.09** g. Two small crops of crystals obtained from the mother liquor resulting from the steam distillation and from the methanol washings weighed **0.15** and **0.21** g., respectively; total yield, **7.45** g., **45.7%** of the calcd. amount.

Anal. Subs., **0.1778, 0.2712: 35.65, 66.4** cc. of **0.05** N $KBrO_3$. Calcd. for $C_6H_4(AsO(OH)_2)_2$: As, **45.99.** Found: As, **45.85, 45.88.**

The identity of the substance was further established by preparation of *o*-phenylenediarsine-oxychloride according to the directions of Kalb.[9] One gram of the diarsonic acid was dissolved in **15** cc. of concentrated hydrochloric acid, treated with **0.5** g. of potassium iodide, and sulfur dioxide passed through the solution for thirty minutes, during which time crystals of o-phenylenediarsine-oxychlorideseparated. Recrysfullization from dilute ethyl alcohol gave crystals which melted at 150°.

Note.—Copper was used as a catalyst at times though its advantages are of doubtful nature. A number of reactions were run without its use and were apparently as good as those run using it; no study of its catalytic properties was made.

The method of arsenic analysis was the potentiometric titration of a digested sample in the presence of an excess of sulfuric acid with potassium bromate, as developed by Cislak and Hamilton, THIS JOURNAL, **52,638 (1930).**

Summary

1. Rosenmund's synthesis of o-carboxyphenylarsonic acid and Albert and Schulenberg's synthesis of *p*-acetophenone-arsonic acid were confirmed.

2. p-Carboxyphenylarsonic acid and o-phenylenediarsonic acid were prepared for the first time by this method, though they have been synthesized previously by other methods.

3. The arseno-test, which consists of warming a saturated solution of an arsonic acid with hypophosphorous acid, seems to be specific for arsonic acids and to be quite sensitive. Its use gave qualitative evidence (together with other considerations) for the formation in small amounts of p-sulfophenylarsonic acid and some unidentified reduced o- and *p*-nitrophenylarsonic acids.

LINCOLN, NEBRASKA

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[9] **Kalb, Ann., 423,** 39 **(1921).**

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE ACTION OF Mg + $MgBr_2$ ON PHENYLBIPHENYLENEMETHYL. THE FORMATION OF PHENYLBIPHENYLENEMETHYLMAGNESIUMBROMIDE

BY W. E. BACHMANN

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Recently it was demonstrated that formation of the Grignard reagent, triphenylmethylmagnesium bromide, takes place through two successive reactions: (a) formation of triphenylmethyl, (b) formation, from that, of the Grignard reagent.[1]

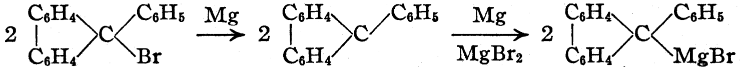
$$2(C_6H_5)_3CBr \xrightarrow{Mg} 2(C_6H_5)_3C + MgBr_2 \qquad (1)$$

$$2(C_6H_5)_3C + Mg + MgBr_2 = 2(C_6H_5)_3CMgBr \qquad (2)$$

Furthermore, it was shown that the free radical itself is quite likely the result of the interaction of Grignard reagent initially produced and unchanged triphenylbromomethane

$$(C_6H_5)_3CMgBr + (C_6H_5)_3CBr = 2(C_6H_5)_3C + MgBr_2 \qquad (3)$$

A similar course is followed by the reaction between phenylbiphenylenebromomethane and magnesium; the rates of reaction in all stages are slower. If a gram atom of magnesium is allowed to react with a gram mole of phenylbiphenylenebromomethane, the Grignard reagent is produced. If, however, only one-half gram atom of metal is employed, phenylbiphenylenemethyl (diphenyl-dibiphenylene-ethane) and magnesium bromide are present at the end of the reaction. If now an additional half atom of magnesium is added to this mixture, the phenylbiphenylenemethyl is converted to the Grignard reagent.



$$2\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>C<\!\!\begin{matrix}C_6H_5\\ \\ Br\end{matrix} \xrightarrow{Mg} 2\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>C\diagup C_6H_5 \xrightarrow[MgBr_2]{Mg} 2\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>C<\!\!\begin{matrix}C_6H_5\\ \\ MgBr\end{matrix} \qquad (4)$$

Phenylbiphenylenemethyl, prepared in various ways, reacts with the system Mg + $MgBr_2$ (or MgI_2) and gives the Grignard reagent. Although diphenyl-dibiphenylene-ethane dissociates only slightly[2] into phenylbiphenylenemethyl radicals, nevertheless, in virtue of this dissociation, the ethane is completely converted to the Grignard reagent.

Since the Grignard reagent was found to react rapidly with phenylbiphenylenebromomethane and give phenylbiphenylenemethyl, it is considered that this is the process whereby the radical is produced as intermediate product in the formation of the Grignard reagent.

Experimental

Phenylbiphenylenemethylmagnesium Bromide.—The 9-phenylfluorenol was prepared from fluorenone and phenylmagnesium bromide according to the directions of

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[1] Gomberg and Bachmann, THIS JOURNAL, 52, 2455 (1930).

[2] Schlenk, Herzenstein and Weickel, Ber., 43, 1754 (1910).

Ullmann and von Wurstemberger.[3] However, a greater yield of product was obtained by hydrolyzing not only the crystalline reaction product but also the solution. In this way from 100 g. of fluorenone there was obtained 140 g. of phenylfluorenol of m. p. 108–109°.

To make the carbinol bromide, 140 g. of carbinol was dissolved in 100 cc. of benzene and 200 g. of acetyl bromide was added. After the solution had been refluxed for twelve hours, most of the solvent was removed under reduced pressure and the residue was treated with an equal volume of petroleum ether. After two recrystallizations from ligroin the phenylbiphenylenebromomethane melted at 99.5–100.5°; yield, 98 g.

Phenylbiphenylenebromomethane (1 Mole) + Magnesium (1 Atom).—Since the Grignard reagent is not very soluble in ethyl ether, the higher boiling n-propyl and n-butyl ethers, mixed with benzene, were employed. All reactions and all operations were carried out in an atmosphere of dry nitrogen. A mixture of 3.22 g. (0.01 mole) of phenylbiphenylenebromomethane and 0.2432 g. (0.01 atom) of magnesium powder in 30 cc. of n-butyl ether and 60 cc. of benzene was heated on a steam-bath. After twelve hours no more magnesium remained and the solution contained glistening crystals of the Grignard reagent. In order to dissolve these crystals an additional 30 cc. of solvent was added. The hot tan-colored solution was filtered and hydrolyzed. The magnesium hydroxide required 9.95 cc. of *N* sulfuric acid for neutralization; calcd., 10.0 cc. From the ether–benzene solution there was isolated 1.8 g. of 9-phenylfluorene, m. p. 146". It was found to be identical with 9-phenylfluorene prepared by reduction of 9-phenylfluorene.[4] Usually a small amount of phenylbiphenylenemethyl peroxide was also found in the hydrolysis product.

Isolation and Analysis of the Grignard Reagent.—A mixture of 3.22 g. of phenylbiphenylenehromomethane and 0.38 g. of magnesium ribbon in 40 cc. of n-butyl ether and 80 cc. of benzene was heated on a steam-bath for twenty-four hours. The clear solution was filtered while hot from the excess of magnesium; 0.235 g. instead of 0.243 g. of magnesium had reacted. On cooling, the filtrate deposited glistening, transparent light yellow plates. These were filtered off, washed with benzene and dried in a stream of nitrogen. For analysis, a half-gram sample was treated with water and the resulting products—phenylfluorene, magnesium hydroxide and brom-ion—were determined. From these results the composition of the compound was calculated on a solvent-free basis.

Anal. Calcd. for $(C_6H_4C_6H_4)(C_6H_5)CMgBr$: $(C_6H_4C_6H_4)(C_6H_5)C$, 69.8; Mg, 7.0; Br, 23.1. Found: $(C_6H_4C_6H_4)(C_6H_5)C$, 69.4; Mg, 7.0; Br, 23.6.

Reaction with Carbon Dioxide.—Dry carbon dioxide was passed for three hours into the Grignard reagent made from 3.22 g. of phenylbiphenylenebromomethane in 45 cc. of ethyl ether–benzene (1:2). At the end of this time a large amount of solid was present. The mixture was hydrolyzed with dilute acid and from the organic solution phenylbiphenylene-acetic acid, $(C_6H_4C_6H_4)(C_6H_5)CCOOH$, was obtained. The product was purified by dissolving it in hot benzene and adding ligroin to the filtered solution. As the solution cooled the acid came out in needles, weight 1.75 g., which represents a 60% yield. As Schlenk and Bergmann[5] report, the phenylbiphenylene-acetic acid readily loses carbon dioxide on being heated and gives phenylfluorene. Because of this decomposition the melting point of the acid varies between 190 and 198°, the value obtained depending upon the rate of heating and the purity of the acid. A sample of the impure acid was converted to phenylfluorene when an attempt was made to recrystallize the acid from glacial acetic acid.

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[3] Ullmann and von Wurstemberger, *Ber.*, **37**, 73 (1904).

[4] Ullmann and von Wurstemberger, ibid., **37**, 74 (1904).

[5] Schlenk and Bergmann, Ann., 463,203 (1928).

Phenylbiphenylenemethyl

Phenylbiphenylenebromomethane (1 Mole) + Magnesium (0.5 Atom).—A mixture of 3.22 g. of phenylbiphenylenebromomethane and 0.1216 g. of magnesium powder in 120 cc. of solvent was heated on a steam-bath. After a time colorless crystals of phenylbiphenylenemethyl began to deposit. As soon as all of the metal had disappeared (five hours), water was added to the mixture. One-half cc. of N acid was needed for the magnesium hydroxide; this indicated the presence of a small amount of Grignard reagent; in agreement with this 0.3 g. of phenylfluorene was found. The radical formed in the reaction was oxidized to the peroxide by allowing the organic solution to evaporate in an open dish. After recrystallization from benzene the phenylbiphenylenemethyl peroxide weighed 1.5 g. (after benzene of crystallization had been removed); m. p. 197°. The compound was found to be identical with the peroxide prepared by the action of molecular silver on phenylbiphenylenechloromethane in presence of air.[6]

Phenylbiphenylenemethylmagnesium Bromide + **Phenylbiphenylenebromomethane.**—To a solution of Grignard reagent prepared from **3.22** g. of phenylbiphenylenebromomethane there was added 3.22 g. of the carbinol bromide. Colorless crystals of phenylbiphenylenemethyl began to precipitate immediately (see Equation 3), and after a few minutes a large amount was present. The mixture was warmed for fifteen minutes and then hydrolyzed with dilute acid. The radical was filtered off in a stream of nitrogen, washed well with acetone and dried; weight 2.3 g.; m. p. 253–254° in a sealed tube filled with carbon dioxide. From the filtrate, additional radical in the form of its peroxide was isolated as well as about half a gram of phenylfluorene.

Phenylbiphenylenemethyl + **Mg** + **$MgBr_2$.**—The radical was prepared in various ways: by the reaction represented in Equation 3; by treatment of the carbinol bromide or chloride with molecular silver or with copper powder in benzene solution. A solution of $MgBr_2$ prepared from 0.5 g. of magnesium powder and 3.6 g. of $HgBr_2$[7] in 30 cc. of ether–benzene (2:1) was filtered into a flask containing 2.0 g. of crystalline phenylbiphenylenemethyl, 1.0 g. of magnesium, 20 cc. of n-propyl ether and 20 cc. of benzene. The resulting mixture was refluxed for sixteen hours. During this time the crystals of radical disappeared and in their place crystals of Grignard reagent appeared. These crystals were brought into solution by addition of more solvent and the solution was filtered; as the filtrate cooled, the glistening crystals of the Grignard reagent again appeared. The crystals were filtered off and analyzed in the same manner as previously described; they were found to have the composition $(C_6H_4C_6H_4)(C_6H_5)CMgBr$. Hydrolysis of the reaction product yielded 1.54 g. of 9-phenylfluorene.

Phenylbiphenylenemethyl + Mg + **MgI_2.—A** mixture of Mg + MgI_2 was prepared from 1.5 g. of iodine and 1 g. of magnesium in 30 cc. of n-propyl ether and 60 cc. of benzene. To the colorless mixture was added 2.41 g. of crystalline phenylbiphenylenemethyl. On heating, reaction started almost at once. When the reaction was at an end, the solution was filtered from the excess of magnesium; 0.125 g. of metal had reacted, calcd. 0.122 (Equation 2). The Grignard reagent produced in the reaction was treated with carbon dioxide for three hours; from the reaction product 2.48 g. of pure phenylbiphenylene-acetic acid was obtained, which represents a yield of 87%.

9,9-Diphenylfluorene from **Phenylmagnesium** Bromide and **Phenylbiphenylenechloromethane.—An** attempt was made to prepare phenylbiphenylenemethyl by the reaction recently described by Schmidt-Nickels,[8] who allowed phenylmagnesium bromide to react with phenylbiphenylenechloromethane. Following his directions, there was obtained 9,9-diphenylfluorene instead of the free radical,

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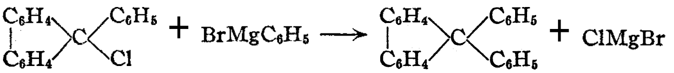
[6] Gomberg and Cone, *Ber.*, 39, 2969 (1906).

[7] Gomberg and Bachmann, THIS JOURNAL, 49, 2586 (1927).

[8] Schmidt-Nickels. ***Ber.***, 62, 917 (1929).


(5)

To the Grignard reagent from 12 g. of bromobenzene there was added 15 g. of 9-chloro-9-phenylfluorene. A vigorous reaction took place, with evolution of a considerable amount of heat, and with precipitation of a white solid as Schmidt-Nickels reports. After the mixture was refluxed for an hour, this solid was filtered off, washed with water and with acetone and then dried; weight 3.1 g.; m. p. 215–220°. After recrystallization from benzene it was obtained in the form of large needles melting at 219–220°, which were found to be identical with 9,9-diphenylfluorene prepared from *o*-phenyltriphenylcarbinol by dehydration.[9]

Summary

The system Mg + $MgBr_2$ (or MgI_2) reacts with phenylbiphenylenemethyl and gives the Grignard reagent, phenylbiphenylenemethylmagnesium bromide, $2(C_6H_4C_6H_4)(C_6H_5)C + Mg + MgX_2 = 2(C_6H_4C_6H_4)(C_6H_5)CMgX$.

The same Grignard reagent is formed from the action of magnesium on phenylbiphenylenebromomethane. This reaction was found to take place in two successive stages: (a) formation of phenylbiphenylenemethyl and $MgBr_2$; (b) reaction of the radical with Mg + $MgBr_2$.

The Grignard reagent was isolated in crystalline state and found to have the composition assigned to it. The compound was converted by water into phenylfluorene, by carbon dioxide into phenylbiphenylene-acetic acid.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE SUPPOSED EXISTENCE OF TWO STEREOISOMERIC 9-BENZYL-9-PHENYLFLUORENES

BY W. E. BACHMANN

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Among the examples of a new kind of stereoisomerism, Schlenk and Bergmann[1] report an isomer of 9-benzyl-9-phenylfluorene. The latter compound was prepared by Gomberg and Cone[2] from benzylmagnesium chloride and 9-chloro-9-phenylfluorene; their product crystallized in prisms and melted at 136°. Schlenk and Bergmann allowed benzyl chloride to react with 9-sodium-9-phenylfluorene and obtained leaflets melting at 125–126°, which they consider to be a stereoisomeric 9-benzyl-9-phenylfluorene. Recently, however, Schmidt, Stein and Bamberger[3] were unable to obtain this isomer when following the directions given for

[9] Ullmann and von Wurstemberger, *Ber.*, 38, 4106 (1905); Clarkson and Gomberg, THIS JOURNAL, 52, 2881 (1930).

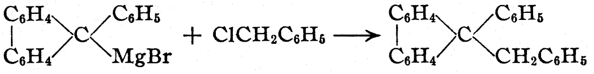
[1] Schlenk and Bergmann, *Ber.*, 62, 745 (1929).

[2] Gomberg and Cone, *ibid.*, 39, 2968 (1906).

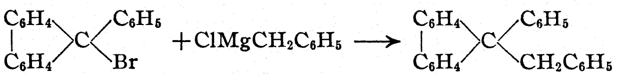
[3] Schmidt, Stein and Bamberger, *ibid.*, 62, 1890 (1929).

its preparation. In phenylbiphenylenemethylmagnesium bromide[4] we have a close analog of the sodium derivative of Schlenk and Bergmann, and its reaction with benzyl chloride was studied in order to determine whether a low-melting compound would be formed when using it instead of the sodium derivative.

Phenylbiphenylenemethylmagnesium bromide reacts readily with benzyl chloride and gives 9-benzyl-9-phenylfluorene


(1)

This compound was found to be identical with the product obtained from benzylmagnesium chloride and 9-chloro- or 9-bromo-9-phenylfluorene


(2)

The product crystallized from ligroin in the form of prisms and melted at 138–138.5°.

The directions of Schlenk and Bergmann were then followed in an attempt to prepare the isomer. However, from 9-sodium-9-phenylfluorene and benzyl chloride there was obtained a *99% yield* of the high-melting compound; no trace of a low-melting isomer was found. The compound was identical in melting point and in crystal form[5] with the products obtained above (Equations 1 and 2).

Experimental

Benzylmagnesium Chloride + 9-Bromo-9-phenylfluorene.—To a filtered solution of benzylmagnesium chloride prepared from 10 g. of benzyl chloride, 8 05 g. of 9-bromo-9-phenylfluorene was added The mixture was heated for six hours and then hydrolyzed. From the ether solution was obtained 5 g. of 9-benzyl-9-phenylfluorene. After recrystallization from n-propyl alcohol the compound melted at 136–136.5°. The melting point was raised to 138–138.5° (corr. 140.3–140.8") by treatment of an acetic acid solution with a small amount of chromic acid. The color was removed from the product by treatment with concentrated sulfuric acid and the substance was then recrystallized from acetic acid. From ligroin the compound was obtained in the form of large transparent crystals.

Phenylbiphenylenemethylmagnesium Bromide + Benzyl Chloride.—Five grams of benzyl chloride was added to the Grignard reagent prepared from 3.22 g. of 9-bromo-9-phenylfluorene, and the resulting mixture was heated for three hours; during this time a large amount of magnesium chloride precipitated. After hydrolysis, *2* g. of 9-benzyl-9-phenylfluorene was obtained. Recrystallization from ligroin gave large prisms melting at 136–137'. After the chromic acid purification the melting point was 138–138.5° (corr. 140.3–140.8"). The Grignard reagent was also prepared from crystalline phenylbiphenylenemethyl and Mg + $MgBr_2$; with benzyl chloride a product was obtained which after recrystallization from ligroin melted at 137.5–138.0°.

Benzyl Chloride + 9-Sodium-9-phenylfluorene (Method of Schlenk and Berg-

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[4] Bachmann, THIS JOURNAL, 52,3287 (1930).

[5] This comparison was made by Dr. C. B. Slawson of the Mineralogy Department, and thanks are extended to him again at this time.

mann).—Phenylfluorenol methyl ether was prepared according to the directions of Schlenk and Bergmann.[6] However, while they report fluorescence of the solution of the methyl ether, no trace of such fluorescence was shown by our solutions.

Five grams of sodium powder was allowed to react with 10 g. of 9-phenylfluorenol methyl ether in 150 cc. of absolute ether in a sealed flask. In less than half an hour the solution was red in color. When the reaction was complete the mixture was treated with benzyl chloride (3 cc.) until no more red sodium derivative remained. The mixture was hydrolyzed, the ether solution was well washed with water and the solvent was then removed under reduced pressure. The crystalline residue was digested with cold methyl alcohol and filtered; weight 11.10 g.; m. p. 136–136.5°. From the alcoholic filtrate an additional 0.32 g. was isolated, making the total yield equivalent to 99%. After being recrystallized from n-propyl alcohol, acetic acid or ligroin, the crystals melted at 138–138.5° (corr. 140.3–140.8°). When mixed with 9-benzyl-9-phenylfluorene made by the other methods the melting point remained the same.

In another experiment the mixture of the reactants was kept cold, and after hydrolysis the reaction product was obtained by allowing the ether to evaporate at room temperature. Only the compound melting at 138–138.5° was obtained.

Summary

9-Benzyl-9-phenylfluorene as prepared from phenylbiphenylenemethylmagnesium bromide and benzyl chloride is identical with the product formed by interaction of 9-bromo-9-phenylfluorene and benzylmagnesium chloride. Furthermore, the same compound was obtained in 99% yield from the action of benzyl chloride on 9-sodium-9-phenylfluorene, and no low-melting isomer was produced in this reaction.

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[CONTRIBUTION NO. 35 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

STUDIES ON POLYMERIZATION AND RING FORMATION. V. GLYCOL ESTERS OF OXALIC ACID

BY WALLACE H. CAROTHERS, J. A. ARVIN AND G. L. DOROUGH

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Melting points ranging from 110 to 172° have been ascribed to ethylene oxalate.[1] Bischoff,[2] by distillation, prepared a form melting at 142–143°, which he showed to be monomeric. He observed that the melting points of this and higher-melting forms change spontaneously on standing, and he ascribed this change to reversible polymerization but without the support of any comparative molecular weight data. In connection with a study of glycol esters of dibasic acids[3] we have made some further observations

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[6] Schlenk and Bergmann, *Ann.*, 463, 202 (1928).

[1] (a) Bischoff, *Ber.*, 27, 2939 (1894); (b) 40, 2803 (1907); (c) Adams and Weeks, THIS JOURNAL, 38, 2518 (1916); *(d)* Tilitcheev, *Ber.*, 56, 2218 (1923).

[2] Bischoff, *ibid.*, 40, 2803 (1907).

[3] Carothers and Arvin, THIS JOURNAL, 51, 2560 (1929); Carothers and Van Natta, *ibid.*, 52, 314 (1930); Carothers and Dorough, *ibid.*, 52, 711 (1930).

on ethylene oxalate and have also prepared some other alkylene oxalates.

Preparation of Ethylene Oxalate.—The ester was prepared by heating ethylene glycol and ethyl oxalate in a Claisen flask provided with *a* receiver. Alcohol distilled off fairly rapidly when the heating bath was kept at 180–190°. The residue was heated in a vacuum for a time to remove unchanged reactants. The distillate was found to contain some ethyl (β-hydroxyethyl) oxalate.

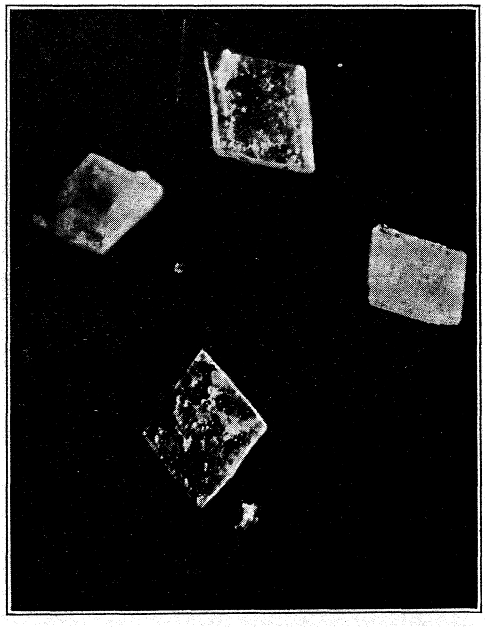


Fig. 1.—Crystals of monomeric ethylene oxalate. X 94. (These crystals were placed for observation in a microscopic culture plate and sealed against the access of air and moisture by means of *a* cover glass. Mechanical disturbances were avoided, and subsequent observations, except the last, were made from exactly the same position as the first.)

Ethyl (β-Hydroxyethyl) Oxalate.—Colorless liquid; b. p. (0.3 mm.), 108–110°; d_4^{20} 1.2241; n_D^{20} 1.4405.

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.42; H, 6.22. Found: C, 44.01; H, 6.02.

The residue after crystallization from glacial acetic acid or from ethyl oxalate was a dusty white powder that usually melted at about 153°. This material was polymeric.

Anal. Calcd. for $C_4H_4O_4$: C, 41.38; H, 3.45; mol. wt., 116; saponification equivalent, 58. Calcd. for $C_{54}H_{58}O_{53} = C_2H_5O—(CO—CO—O—(CH_2)_2—O)_{13}H$: C, 41.70; H, 3.73; mol. wt., 1554; saponification equivalent, 59.4. Found: C, 41.66, 41.97; H, 3.76, 4.05; mol. wt. (in boiling acetonitrile), 1510, 1580, 1610; saponification equivalent, 59.0, 60.8, 61.0.

When this polymer was heated in a vacuum, distillation occurred and from the distillate Bischoff's 143° ester was obtained (observed m. p., 143–144°). Molecular weight determinations in boiling acetonitrile agreed with those in freezing acetic acid reported by Bischoff, indicating that this material is monomeric.

Anal. Calcd. for $C_4H_4O_4$: C, 41.38; H, 3.45; mol. wt., 116. Found: C, 41.42, 41.44; H, 3.66, 3.45; mol. wt. (in boiling acetonitrile), 118, 120, 123, 126.

Small samples of polymer, if distilled rapidly, gave better than 50% yields of the monomer. Under other conditions the yield was smaller owing to thermolysis[1d] to ethylene, carbon dioxide, ethylene carbonate, carbon monoxide and other gaseous, liquid and tarry products.

Properties of Ethylene Oxalate and its Polymers.—Monomeric ethylene oxalate is definitely macrocrystalline and shows a relatively high solubility (Table II). It is so readily hydrolyzed that it may be titrated directly with warm tenth normal alkali. On standing at room temperature, the sharply defined crystals of the monomer rapidly disintegrate (Figs. 1–3) with the appearance of having been violently disrupted, and finally are transformed into very minute crystals, which, if undisturbed, may become spontaneously oriented on a glass surface to thread-like aggregates (Fig. 4).

This transformation is due to polymerization. It is accelerated by moderate heat and catalyzed by acids or alkalies. The polymerization is accompanied by changes in melting point and solubility. In the first stages of the polymerization the melting point drops (*e.* g., to 106–110°); higher-melting polymers are formed by heating the monomer in the presence or absence of solvents or catalysts, and the final product is an insoluble material melting at 172–173°.

Fig. 2.—The crystals of Fig. 1 after five days at room temperature. X 94.

A sample of monomeric ethylene oxalate was heated at 135–140° for seven hours, and then extracted repeatedly with cold acetone. The material that separated on evaporation of the acetone was identified as unchanged monomer. The acetone-insoluble material was a dusty white powder which after drying melted at 171–172°. It was insoluble in all common organic solvents, so no molecular weight determinations could be made.

Anal. Calcd. for $(C_4H_4O_4)_x$: C, 41.38; H, 3.45; saponification equivalent, 58.0. Found: C, 41.48, 41.59; H, 3.71, 3.96; saponification equivalent, 58.45.

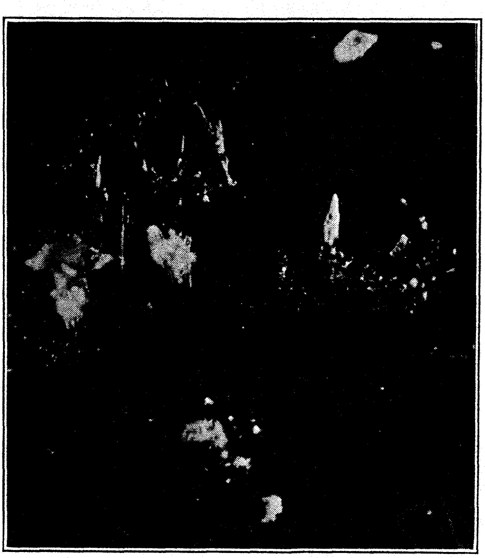
By fractional crystallization of polymerized monomer and of the 153° polymer formed directly from glycol and oxalic ester, a great variety of samples was obtained showing such melting points as 106–108°, 122–125°, 140–142°, 148–150°, 153°, 155–157°, 157–159°, 160–163°, 163–164°, 172–173°, as well as others having much wider melting ranges. Attempts to segregate homogeneous samples from these fractions met with difficulties due to the rapidity with which spontaneous transformations occurred even in the absence of solvents and at room temperature. Portions of three sharply melting samples were stored in glass-stoppered bottles, and melting point determinations were made at intervals with the following results.

TABLE I

MELTING POINTS

Nature and m. p. of sample	M. p. after standing at room temperature 2 months	 4 months	 $5^1/_2$ months
144° (monomer)	105-140°	105–135°	105–122° (A)
153° (polymer)	149–155°	149–155°	149–155" (B)
172° (polymer)	160–170°	160–170°	160–170° *(C)*

To avoid these changes during the process of fractionation, it was necessary to work rapidly and to use cold solvents as far as possible. Solubility data established the homogeneity of the monomer **(144')** and the apparent homogeneity of the highest **(172')** polymer. Intermediate fractions, unlike the 172° polymer, were completely soluble in warm acetonitrile, and since the solubility of the latter was not affected by the presence of monomer, intermediate polymers must have been present in these fractions. This led to the hope that it might be possible to isolate polymers sufficiently low for **a** study of structure.



Pig. 3.—The crystals of Fig. 1 after seven days at room temperature. X 113.

The fractions A, B and C of Table I were recrystallized with the following results: extraction of A with cold acetone removed a small amount of monomer. The residue was treated with warm acetonitrile, which dissolved all but a small amount of material that melted at 170–172° (high polymer). The material that separated from the acetonitrile solution, after recrystallization, melted at 157–159°. Similarly from **B,** fractions were isolated corresponding with monomer, high (172°) polymer, and 157–159° polymer. **C** yielded a small amount of material melting at 155–157°. The rest was unchanged 172° polymer. Extractions of various other samples were made, and in one case a small fraction melting at 106–108° and having an apparent molecular weight of about **900** was isolated.

There is still considerable doubt, however, concerning the homogeneity of this fraction.

The 153° material, which was the usual (recrystallized) product of the action of ethylene glycol on ethyl oxalate, was not homogeneous in spite of its fairly sharp melting point, for its apparent solubility changed with changing ratio of solute to solvent as shown below.

Sample, g.	Acetonitrile, cc.	Apparent soly. in g. per 100 g. at 25°
0.025	15	0.0821
.100	15	.2633
.500	15	.8644

A four-gram sample of the 153° material was then extracted repeatedly with 25-cc. portions of acetonitrile. With each extraction the apparent solubility decreased until a constant value was reached.

Extraction number	Apparent soly. in g. per 100 g. at 25°	M. p. of residue, °C.
1	1.4321	152–153
2	0.8111	152–155
3	.3240	155–159
4	.2390	155–160
5	.1729	157–160
6	.1315	157–159
7	.0894	157–159
8	.0891	158–159
9	.0890	158–159

The apparent solubility of the residue did not change on increasing the ratio of solute to solvent five-fold, so this material must be regarded as essentially homogeneous. Its apparent molecular weight in boiling acetonitrile was about 2380 (observed values, 2070, 2480, 2670, 2370, 2275, 2520).

One may conclude that at least two polymers of ethylene oxalate exist: a soluble form melting at 158–159° of molecular weight about 2400, and an insoluble form melting at 172° of unknown but probably much higher molecular weight. Either of these forms may arise spontaneously from the other, and both of them may be formed from the monomer. Definite evidence for the existence of other polymers of ethylene oxalate is lacking.

TABLE II

SOLUBILITIES OF ALKYLENE OXALATES

Nature of oxalate sample	M. p., °C.	Observed mol. wt.	Solvent Acetonitrile	 Acetone	 Chloroform
Monomeric ethylene	144	118–126	1129	4.13	0.35
Polymeric ethylene	159	2070–2670	0.0891	.....	.....
Polymeric ethylene	172	....	<0 01	<0.01	<0.01
Monomeric propylene	142	131–147	12.31	3.47	0.06
Monomeric ethylene heated at 90° for two weeks	148–150	1620–1640	0.1823[a]	0.1630[a]	0.0390[a]

[a] These values have no quantitative significance since the sample was not homogeneous.

Chemical Properties of the Polymeric Ethylene Oxalates.—Monomeric ethylene oxalate is hydrolyzed with extraordinary rapidity. To a certain extent this property is shared by its polymers. Hence, although the polymers show acid reactions toward litmus in contact with water, this fact cannot be used to argue for the presence of long primary valence chains bearing carboxyl groups at the end. Attempts to prepare sodium salts from the polymers by the action of cold sodium bicarbonate solution led to the isolation of sodium oxalate and unchanged polymer. This ease of hydrolysis is associated with great sensitivity toward other reagents. The attempt to detect hydroxyl groups or carboxyl groups by heating polymeric ethylene oxalate with *m*-bromobenzoic anhydride and with phenylhydrazine led to the isolation of ethylene-*bis*-*m*-bromobenzoate and to the phenylhydrazide of oxalic acid. The latter reaction is what would be expected from an ester having the structure —CO—CO—O—$(CH_2)_2$—O—CO—CO—O—$(CH_2)_2$—O—, etc., whether the chain is open or closed, but the first reaction requires the elimination of —CO—CO—O— residues. These fragments of the molecules appeared as carbon monoxide and carbon dioxide, which were observed to be evolved from the reaction mixture.

Fig. 4.—The crystals of Fig. 1 after two weeks at room temperature. X 185.

Ethylene *bis*-*m*-Bromobenzoate.—Prepared by the action of m-bromobenzoic anhydride on ethylene glycol or on ethylene oxalate; crystallized from a mixture of chloroform and alcohol; m. p. 78–79°.

Anal. Calcd. for $C_{16}H_{12}O_4Br_2$: C, 44.86; H, 2.80; Br, 37.38; mol. wt., 428. Found: C, 44.85, 45.06; H, 2.92, 2.98; Br, 37.26, 37.03; mol. wt. (in boiling benzene), 430.

Propylene Oxalate.—By heating propylene glycol and ethyl oxalate together and removing unchanged reactants in a vacuum, a colored viscous resin was obtained. In boiling acetonitrile this showed an apparent molecular weight of about 700 (observed, 670, 660). No crystalline material could be isolated from it. When this resin was strongly heated at a pressure of 5 mm., distillation occurred. A crystalline solid that separated from the liquid distillate melted at 142° after recrystallization from hot alcohol. This was identified as monomeric propylene oxalate.

Anal. Calcd. for $C_5H_6O_4$: oxalic acid, 69.24; saponification equivalent, 65; mol. wt., 130. Found: oxalic acid, 69.82; saponification equivalent, 64.5, 65.1; mol. wt. (in boiling acetonitrile), 131,147.

Carbon and hydrogen values (Pregl method) were consistently low, perhaps owing to the loss of methane.

The monomeric methyl ethylene oxalate showed no tendency to polymerize spontaneously at room temperature, but on being heated to 140–150° for eight hours it was converted to a white powder that melted at 176–178° and was insoluble in all common organic solvents.

Trimethylene Oxalate.—This ester has been prepared by Tilitcheev[4] as a solid melting at 82–84° by heating methyl oxalate with trimethylene glycol first at atmospheric and then under diminished pressure, dissolving the residue in chloroform, and precipitating it with methyl alcohol. On distillation at 3–4 mm. pressure it was converted into an "isomeric" form melting at 186–187°.

Since the length of the chain of the structural unit of trimethylene oxalate is seven atoms, the reaction between oxalic ester and trimethylene glycol should be intermolecular and the product polymeric, in accordance with the generalization based on the study of other similar reactions.[5,3]

We prepared trimethylene oxalate" by heating ethyl oxalate with trimethylene glycol. After three crystallizations from a mixture of chloroform and ethyl alcohol it melted at 87–88'. Its apparent molecular weight in boiling acetonitrile was about 2000 (observed value, 2040, 1980).

Anal. Calcd. for $C_5H_6O_4$: C, 46.15; H, 4.65. Found: C, 46.03, 46.34; H, 4.90, 4.95.

When this polymeric material was heated at 250° at 3 4 mm., thermolysis and distillation occurred. Gaseous, liquid and carbonaceous products were formed. The liquid distillate from 52 g. of polymer weighed 23.6 g., and on being cooled and treated with alcohol it yielded a small amount of crystalline solid, which after repeated crystallization melted at 186–187°. This was Tilitcheev's "isomeric" trimethylene oxalate.

Anal. Calcd. for $(C_5H_6O_4)_2$: C, 46.15; H, 4.65; mol. wt., 260. Found: C, 45.75, 46.12; H, 4.61, 4.69; mol. wt. in boiling acetonitrile, 282, 278; in freezing phenol, 272, 265.

The molecular weight determinations prove this material to be dimeric.

The liquid distillate from which the dimeric trimethylene oxalate was isolated was redistilled. It boiled from 70° at 20 mm. to 185° at 0.25 mm. From the higher-boiling fractions a considerable amount of trimethylene

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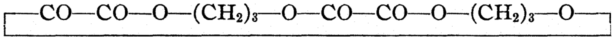
[4] Tilitcheev, J. *Russ. Phys.-Chem. Soc.*, *58, 447* (1926); *C.* A., 21, 3358 (1927); *Chem. Zentr.*, II, 440 (1927).

[5] Carothers, THIS JOURNAL, 51,2548 (1929).

carbonate was isolated. This is a product that Tilitcheev assumed to be intermediate in the thermolysis of trimethylene oxalate, but he was unable to isolate it. Saponification of the remaining liquid led to the isolation (as calcium oxalate) of about 1.5 g. of oxalic acid. Hence it is possible that some monomeric trimethylene oxalate may have been present in the mixture.

These results lead to the following conclusions. The action of trimethylene glycol on ethyl oxalate proceeds intermolecularly and leads to an ester of the type —CO—CO—O—$(CH_2)_3$—O—CO—CO—O—$(CH_2)_3$—O—CO—CO—O—$(CH_2)_3$—O— etc. This on being heated to a high temperature undergoes thermal decomposition and yields a complicated mixture of products containing a small amount of the 14-membered cyclic ester



$$\text{—CO—CO—O—}(CH_2)_3\text{—O—CO—CO—O—}(CH_2)_3\text{—O—}$$

These reactions are analogous to those observed in the formation and decomposition of ethylene succinate[6] and tetramethylene carbonate.' No truly reversible relationship between a monomeric and polymeric form of trimethylene oxalate exists, as it does in ethylene oxalate and in trimethylene carbonate.[7] The dimeric trimethylene oxalate shows no tendency to polymerize spontaneously.

Hexamethylene Oxalate and Decamethylene Oxalate.—From considerations which have already been set forth it is to be expected that these esters, by whatever method they are prepared, will be linear condensation polymers. They are readily prepared by heating ethyl oxalate with the corresponding glycols at first under atmospheric pressure and finally in high vacuum.

Hexamethylene Oxalate.—White powder purified by precipitation from chloroform by methyl alcohol, m. p. 66°.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.79; H, 7.03; mol. wt., 172. Found: C. 55.77, 55.58; H, 7.17, 7.08; mol. wt. (in boiling benzene), 1050, 1160, 1120.

Decamethylene Oxalate.—White powder purified by precipitation from chloroform by methyl alcohol, m. p. 79°.

Anal. Calcd. for $C_{12}H_{24}O_4$: C, 62.57; H, 9.63; mol. wt., 232. Found: C, 62.89, 62.73; H, 8.97, 8.90; mol. wt. (in boiling benzene), 1160, 1190.

Summary

Ethylene oxalate exists in three mutually interconvertible forms: a monomer (m. p. 144°), a soluble polymer (m. p. 159°), and an insoluble polymer (m. p. 172°). Ethylene oxalates showing other melting points are probably mixtures of these three forms, since evidence for the existence of any other individual forms is lacking. None of these forms are stable at ordinary temperature. The monomer polymerizes spontaneously, and the purified polymers are partially depolymerized.

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[6] Carothers and Dorough, THIS JOURNAL, 52, 718 (1930).

[7] Carothers and Van Natta, *ibid.*, 52,314 (1930).

Propylene oxalate exists in at least two mutually interconvertible forms: a monomer and a polymer. Monomeric propylene oxalate polymerizes much less rapidly than ethylene oxalate.

Trimethylene oxalate (m. p. 86°) prepared from ethyl oxalate and trimethylene glycol is a linear condensation polymer. It shows no tendency to depolymerize spontaneously. At high temperature it undergoes thermal decomposition, and one of the products of this reaction is the dimeric 14-membered heterocycle, m. p. 187°. This is stable and shows no tendency to polymerize further.

Hexamethylene oxalate and decamethylene oxalate prepared by the action of the glycols on ethyl oxalate are linear condensation polymers.

Ethyl(*p*-hydroxyethyl)-oxalate and ethylene-bis-m-bromobenzoate are described.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF McLAUGHLIN GORMLEY KING COMPANY]

STUDIES ON PYRETHRUM FLOWERS. IV. THE RELATIVE TOXICITY OF PYRETHRINS I AND II

BY C. B. GNADINGER AND C. S. CORL

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Staudinger and Harder[1] have shown that the two pyrethrins do not occur in *Pyrethrum* flowers in equal proportions. This conclusion has been confirmed by Tattersfield and Hobson.[2] The amount of pyrethrin II, in the flowers examined by these writers, was from 38 to 172% of the pyrethrin I content. If the two pyrethrins are equally toxic to insects, the proportion in which they are present is of little importance, and a determination of the total pyrethrin content would indicate the toxic value of a given sample. If, however, there is a considerable difference in the toxicity of the two pyrethrins, it would be necessary to determine the proportion of each present in a sample in order to establish its insecticidal value.

Staudinger and Ruzicka[3] state that pyrethrin I is somewhat more toxic than pyrethrin II. Gnadinger and Corl[4] also found that pyrethrin I is slightly more toxic. Tattersfield, Hobson and Gimingham[5] found that pyrethrin I is about ten times more toxic than pyrethrin II, and they attempted to prove that the toxicity of *Pyrethrum* flowers depends almost entirely on the pyrethrin I content.

In view of the contradictory conclusions reached by different investi-

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[1] Staudinger and Harder, *Ann. acad. sci. Fennicae*, **29A**, 1–14 (1927).

[2] Tattersfield and Hobson, *J. Agr. Sci.*, 19, 433–437 (1929).

[3] Staudinger and Ruzicka, *Helv. Chim. Acta*, 7, 449 (1924).

[4] Gnadinger and Corl, THIS JOURNAL, 51, 3054 (1929).

[5] Tattersfield, Hobson and Gimingham, *J. Agr. Sci.*, 19, 266–296 (1929).

gators, it was considered advisable to isolate the pyrethrins and determine their toxicity by the most accurate biological method available. At the same time the toxicity of *Pyrethrum* flowers assayed by the method of Gnadinger and Corl[4] was determined, thus deciding whether or not this method is a true measure of the toxicity to insects.

Through the courtesy of Mr. E. B. Phillips, Chief Chemist, the biological experiments were conducted at the laboratory of the Sinclair Refining Company, East Chicago, Indiana. This company was invited to take part in the work because of its experience in testing *Pyrethrum* insecticides biologically, and because its facilities for this work are unexcelled. The experiments were carried out under the supervision of Mr. N. J. Gothard, Assistant Chief Chemist, and Mr. A. G. Grady, Entomologist. We express our appreciation to the Sinclair Refining Company, Mr. Phillips and his assistants; without their cooperation the work could not have been completed.

Experimental

Isolation of Pyrethrins I and II.—The isolation of pyrethrin I from *Pyrethrum* flowers by the method of Staudinger and Ruzicka[6] is not particularly difficult. It should be noted, however, that neither Staudinger and Ruzicka nor Tattersfield, Hobson and Gimingham isolated pyrethrin II direct from the flowers. Instead, they saponified a mixture of the semicarbazones of pyrethrin I and II, obtaining eventually, after appropriate treatment, the alcohol pyrethrolon and the two acids, chrysanthemum monocarboxylic acid and chrysanthemum dicarboxylic acid methyl ester. Part of the pyrethrolon and the monocarboxylic acid were esterified to form pyrethrin I and another portion of the pyrethrolon was combined with the dicarboxylic acid methyl ester to yield pyrethrin II. Staudinger and Ruzicka[7] have pointed out that these partially synthesized pyrethrins do not yield semicarbazones of sharp melting point, and suggest that a change has possibly taken place in the side chain of the pyrethrolon or that stereoisomers are present. Tattersfield, Hobson and Gimingham[5] also mention that their synthetic pyrethrin II possibly contained an isomer which lowered the toxicity. Gnadinger and Corl[4] were able to isolate the semicarbazone of pyrethrin II directly from the flowers in fairly pure condition by repeated crystallization of the mixed semicarbazones of pyrethrin I and II.

For the present work, 215 kg. of Japanese *Pyrethrum* flowers was treated in substantially the manner described by Staudinger and Ruzicka.[6] About 500 g. of white, crystalline, mixed semicarbazones of pyrethrin I and II, melting at 60–90° was obtained. This material was repeatedly crystallized from 90% alcohol, 60% alcohol and a mixture of one part benzene and three parts of petroleum ether, In this way were obtained 40 g. of pyreth-

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[6] Ref. 3, p. 184.

[7] Ref. 3, pp. 451453.

rin I semicarbazone melting at 115–117° and 30 g. of pyrethrin II semicarbazone, melting point 55–61°. Further crystallization of the latter finally yielded a product melting at 54–58' whose melting point was not lowered by further crystallization. In addition, a large quantity of mixed semicarbazones of pyrethrin I and II was obtained.

Purity of the Semicarbazones.—About 1 g. of the pyrethrin I semicarbazone, melting at 115–117°, was saponified by boiling with a solution of 1 g. of sodium hydroxide in 100 cc. of 90% methanol. The alkaline solution was then acidified with sulfuric acid and distilled with steam. The chrysanthemum monocarboxylic acid in the distillate was determined by titration and from this the percentage of pyrethrin I semicarbazone in the original material was calculated. The chrysanthemum dicarboxylic acid in the residue from the steam distillation was determined by extracting with ether and titrating the residue obtained by evaporating the ether solution. Blanks were run on the reagents. In the same manner, the percentage of pyrethrin I semicarbazone in the pyrethrin II semicarbazone melting at 54–58' was determined.

Analysis of pyrethrin I semicarbazone	
Volatile acids calculated as pyrethrin I semicarbazone	96.94%
Non-volatile acids calculated as pyrethrin II semicarbazone	8.10%
Analysis of pyrethrin II semicarbazone	
Volatile acids calculated as pyrethrin I semicarbazone	16.94%

The pyrethrin I semicarbazone was 97% pure, while the pyrethrin II semicarbazone contained 17% of semicarbazone of pyrethrin I. The total acidity found in the analysis of pyrethrin I semicarbazone was 5% higher than the theoretical amount. This is probably due to the formation of acid compounds by the action of the sodium hydroxide on pyrethrolon semicarbazone. Staudinger and Ruzicka[8] found that pyrethrolon yielded dehydropyrethrolon, a compound having weak acid properties, on prolonged digestion with alcoholic sodium hydroxide.

Purity of the Isolated Pyrethrins.—The semicarbazones were converted into the pyrethrins by digestion with oxalic acid solution.[9] The crude pyrethrins so obtained were extracted with petroleum ether and the petroleum ether solution was washed once with 10% potassium carbonate solution, three times with 1% sodium hydroxide, three times with water, three times with 3% potassium permanganate, three times with water, once with 1% sodium hydroxide and three times with water. It was then filtered and distilled *in vacuo* to constant weight at a maximum temperature of 40°.

The monocarboxylic acid in the pyrethrin I was determined as previously

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[8] Ref. 3, p. 220.

[9] Ref. 3, p. 194.

described, by saponification and distillation with steam, and was calculated to pyrethrin I. The percentage of pyrethrin I was also determined from the copper reducing power.[4]

Analysis of pyrethrin I

Pyrethrin I calculated from volatile acid	79.7%
Pyrethrin I calculated from copper reducing power	79.5%

Anal. Calcd. for $C_{21}H_{30}O_3$: C, 76.31; H, 9.16. Found: C, 76.51, 76.20; H, 9.06, 8.89.

Similarly the amounts of monocarboxylic acid and dicarboxylic acid in the pyrethrin II were determined and calculated to pyrethrin I and II, respectively.

Analysis of pyrethrin II

Pyrethrin I calculated from volatile acid	23.3%
Pyrethrin II calculated from non-volatile acid	84.3%

Anal. Calcd. for $C_{22}H_{30}O_5$: C, 70.54; H, 8.08. Found: C, 72.62, 72.00; H, 8.17, 8.09.

The pyrethrin I was 80% pure and contained little pyrethrin II. The ultimate analysis, however, showed practically the theoretical percentage composition for pyrethrin I. The pyrethrin II contained about 20% pyrethrin I and 80% pyrethrin II. As in the analysis of the pyrethrin I semicarbazone, the total acidity was about 7% higher than the theoretical, probably because of the presence of acid decomposition products of pyrethrolon. Ultimate analysis confirmed that the material was a mixture of about 20% pyrethrin I and 80% pyrethrin II.

Preparation of Solutions for Biological Experiments.—Solutions of pyrethrin I and pyrethrin II were prepared by dissolving the accurately weighed pyrethrins in a highly refined mineral oil. These solutions were made within twelve hours from the time the pyrethrins were isolated and in the interval the latter had been kept in vacuum flasks. These precautions were taken to insure that the pyrethrins were not oxidized by exposure to the air. The mineral oil used was water white, nearly odorless and tasteless; specific gravity 0.785 at 15.6°; distilling range, 180–240°. The pyrethrin solutions were perfectly clear and were colorless. Solutions were prepared containing 150, 125, 100, 75, 50, 25 and 10 mg. of the isolated pyrethrins per 100 cc. The actual amounts of pyrethrins in these solutions were calculated from the analyses given above, which showed that the pyrethrin I was 80% pure and the pyrethrin II consisted of 77% pyrethrin II and 23% of pyrethrin I.

Extracts were prepared from four samples of Pyrethrum flowers, which had been assayed by the method of Gnadinger and Corl, using the same oil employed for making the pyrethrin solutions. The ground flowers were macerated for seventeen days with frequent shaking. The extracts were then filtered and kept in well filled bottles in a dark closet. The composition of these extracts is fully described in Table I.

TABLE I

EXTRACTS OF ASSAYED FLOWERS (*Pyrethrum cinerariaefolium*)

		Pyrethrins			Composition of oil extracts		
No.	Description	6/3/29	1/28/30	Av.	Flowers, g.	Oil, cc.	Pyrethrins, mg. per 100 cc.
6	Dalmatian open, 1926 crop	0.60 .56	0.60	0.59	63.5	497.5	75
7	Dalmatian half open, 1925 crop	.38 .38	.33	.36	69.5	497.3	50
13	Dalmatian open, 1926 crop	.43 .43	.39	.42	59 5	497 6	50
82	Japanese, 1929 crop		.97 .97 .93	.96	104 2	996 0	100

From the extract of sample 6, dilutions were prepared containing 60 and 40 mg. of pyrethrins per 100 cc.; from sample 82, solutions containing 80, 60, 40, 20 and 10 mg. per 100 cc. were made. All of the solutions were kept in the dark when not in use.

Biological Experiments.—Many attempts have been made to evaluate powdered Pyrethrum by actual tests on insects. Flies, roaches, bedbugs, bees, aphids and other insects have been employed for this purpose. The principal causes of error in these tests were lack of uniformity in the vitality of the insects used and inability to apply the same dosage of Pyrethrum powder to each insect. When it is considered that Pyrethrum flowers contain from 100 to 150 times the lethal dose of pyrethrins for these insects, it is not surprsiing that the results were meaningless. The value of these methods is best illustrated by the fact that closed Dalmatian flowers were generally considered superior to open and Japanese flowers even as late as 1929. It is now known that open flowers are more toxic than closed and that Japanese flowers contain about twice the amount of pyrethrins found in Dalmatian flowers.[10]

Within the last three years, however, methods for evaluating the Pyrethrum-oil sprays have been developed which yield good results. Probably the most accurate biological method for evaluating these sprays is the method of Peet and Grady,[11] which, briefly, is as follows.

About 100 flies, five days old, are placed in a chamber 1.83 by 1.83 by 1.83 meters in size, whose walls have been rendered non-absorbent with sodium silicate. The temperature of the chamber is kept at 25.6°. Twelve cc. of Pyrethrum-oil spray is introduced through four one-half inch holes near the ceiling, using a special type of atomizer under a constant pressure of 0.88 kg. per sq. cm. At the end of ten minutes the flies clinging

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[10] Gnadinger and Corl, THIS JOURNAL, 52, 680–688 (1930).

[11] Peet and Grady, *J. Econ. Entomol.*, 21,612 (1928).

to the ceilings and walls are counted and those which have dropped are carefully placed in wire gauze cages containing bread and milk and cheesecloth saturated with water, and are allowed to stand overnight at 25.6° and about 45% humidity. At the end of twenty-four hours, the number of disabled flies that have died or recovered is recorded. Unless water is supplied to the disabled flies, nearly all will die regardless of the toxicity of the spray. As soon as the flies have been removed from the test chamber, the walls are carefully wiped and the chamber is ventilated for twenty minutes by means of a blower and fan which draw air through a number of sliding doors in the chamber; it is then ready for another test.

The flies used in the test are carefully bred for the purpose in an insectary, held at constant temperature and humidity, in substantially the manner described by Grady.[12] By this method flies are available the year round. These flies are more resistant than wild flies, and since the age of each culture is definitely known, the vitality of the flies is more uniform.

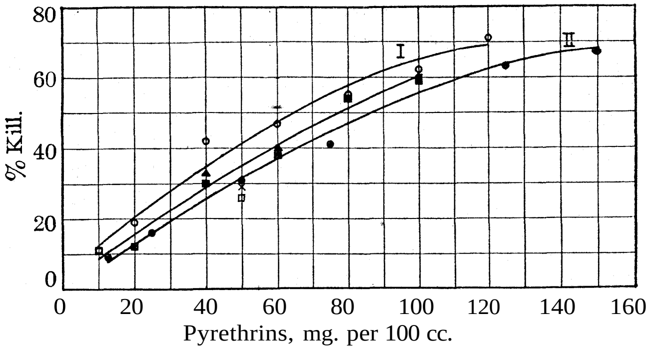

Fig. 1.—Toxicity of pyrethrin I, pyrethrin II and ***Pyrethrum*** flowers to flies. ○, Pyrethrin I; ●, Pyrethrin II; ■, Flowers. No. 82; ▲, Flowers. No. 6; □, Flowers. No. 13; X, Flowers. No. 7.

Thus the method of Peet and Grady controls, as far as possible, the vitality of the insects, temperature, concentration of spray in the test chamber, pressure at which the spray is applied, time the insects are subjected to the action of the spray and humidity.

All of the biological tests presented in Table II were made by Mr. Grady and were observed by one of us. The temperature throughout the experiments was 25.6° and the humidity 43–50%. The same atomizer was used in all experiments. The results of every experiment are recorded with the exception of five which were obviously incorrect. The controls were not sprayed but were kept in the same kind of cage and under the same conditions as the disabled flies. The values for pyrethrin I and pyrethrin

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[12] Grady, J. Econ. *Entomol.*, **21**, 598 **(1928).**

II and Pyrethrum flowers, after correcting for the kill due to the oil alone, are plotted in Fig. 1; the curve of the pyrethrin I solution is based on 100% pure pyrethrin I. The material from which the pyrethrin II curve was prepared consisted of 23% pyrethrin I and 77% pyrethrin II.

Table II

Toxicity of Pyrethrins I and II and Pyrethrum Flowers to Flies (M. *domestica*)

No. of tests	Description of soln.	Pyrethrin content mg. per 100 cc.			Av. no. flies	Disabled in 10 min., av., %[a]	Condition of disabled flies in 24 hrs.			
		I	II	Total			Recovered, av., %[a]	Dead Max., %[a]	Dead Min., %[a]	Dead Av., %[a]
7	Oil only	0	0	0	97	19	15	6	1	4
7	Pyrethrin I	120		120	97	95	20	83	68	75
4	Pyrethrin II	34	116	150	97	99	28	76	66	71
4	Pyrethrin I	100		100	96	95	29	71	57	66
4	Pyrethrin II	29	96	125	99	98	31	73	60	67
6	Flowers No. 82	39	61	100	99	96	33	69	53	63
6	Pyrethrin I	80		80	97	96	33	66	50	63
5	Pyrethrin II	23	77	100	94	97	33	71	57	64
5	Flowers No. 82	31	49	80	95	96	38	67	52	58
3	Pyrethrin I	60		60	98	92	41	52	50	51
3	Pyrethrin II	17	58	75	96	96	51	48	40	45
6	Flowers No. 82	23	37	60	96	94	52	52	33	42
4	Flowers No. 6			60	95	92	48	46	40	44
5	Pyrethrin I	40		40	94	90	44	52	40	46
4	Pyrethrin II	11	39	50	103	93	58	42	29	35
5	Flowers No. 82	16	24	40	93	91	57	44	26	34
4	Flowers No. 6			40	105	82	45	42	30	37
4	Flowers No. 7			50	96	81	47	40	30	34
4	Flowers No. 13			50	95	78	48	38	26	30
3	Pyrethrin I	20		20	98	69	46	29	18	23
3	Pyrethrin II	6	19	25	96	83	63	20	19	20
3	Flowers No. 82	8	12	20	91	76	60	21	13	16
3	Pyrethrin I	10		10	91	50	35	20	8	15
3	Pyrethrin II	3	10	13	101	64	51	17	8	13
3	Flowers No. 82	4	6	10	93	65	50	22	10	15
7	Controls (not sprayed)	0	0	0	92			0	0	0

[a] Per cent. of number of flies used.

Inspection of Table II indicates at once that the difference in toxicity between pyrethrin I and pyrethrin II cannot be great. Calculations from the kill (Fig. 1) at concentrations of 120, 100, 80, 60 and 40 mg. per 100 cc. show that pyrethrin II is at least 77% as toxic as pyrethrin I. The kill obtained with the extract of flowers No. 82 is further proof that pyrethrin II is nearly as toxic as pyrethrin I. Sample No. 82 was analyzed by three different laboratories, both by Tattersfield's method and the method of Gnadinger and Corl. These analyses are given in Table III.

The ratio of pyrethrin I to pyrethrin II in Sample No. 82 is 1:1.5 but the

TABLE III

ANALYSIS OF Pyrethrum FLOWERS NO. 82

Laboratory	Tattersfield method, pyrethrins						Gnadinger and Corl method, total pyrethrins, %	
	I, %		II, %		Total, %			
A	0.39	0.38	0.60	0.60	0.99	0.98	0.92	
B							.95	0.95
C							.97	.97
							.97	.93

kill is only slightly less than with pure pyrethrin I and is somewhat greater than with pyrethrin II. The toxicity of Sample No. 6 is also between that of pyrethrin I and pyrethrin II while the toxicity of Nos. 7 and 13 is about the same as that of pyrethrin II. Therefore the toxicities of oil extracts of Pyrethrum, whose total pyrethrin content has been determined by the copper reduction method, fall between the toxicity of pyrethrin I solution and the toxicity of pyrethrin II solution of the same pyrethrin content, made by dissolving the pyrethrins in the same oil. Furthermore, it will be seen from Tables I and II that when extracts of *Pyrethrum* flowers, of widely different pyrethrin content, are diluted to the same pyrethrin content, as determined by the copper reduction method, the toxicities are substantially the same.

Table II affords an idea of the accuracy of the biological method. It should be noted that the percentage of flies disabled in ten minutes is not an index of the toxicity of the spray.

Summary

1. Pyrethrins I and II of known purity have been isolated directly from Pyrethrum flowers.
2. The toxicity of pyrethrins I and II to house flies (*Musca domestica*) has been determined by the method of Peet and Grady.
3. The toxicity of oil solutions of pyrethrins I and II has been compared with the toxicity of oil extracts of Pyrethrum flowers assayed by the copper reduction method.
4. The comparative toxicity of extracts of Pyrethrum flowers, of widely different pyrethrin content by the copper reduction method, has been determined.
5. Pyrethrin II is approximately 80% as toxic to flies as pyrethrin I.
6. The determination of the total pyrethrin content of *Pyrethrum* flowers by the copper reduction method of Gnadinger and Corl is an accurate index of their toxicity.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM ILLINOIS STATE WATER SURVEY DIVISION]

THE ANAEROBIC OXIDATION OF FATTY ACIDS

BY S. L. NEAVE WITH A. M. BUSWELL

RECEIVED APRIL 25, 1930 PUBLISHED AUGUST 5, 1930

Studies on anaerobic metabolism are of interest not only to explain anaerobiosis in general, but also as guides to the early steps in the series of organic transformations constituting aerobic respiration. Among the facultative anaerobes, there is no proof that the initial changes undergone by a food material on entering the cell are governed by free oxygen. In animal biochemistry, also, recent progress has emphasized the role of organic molecules as hydrogen donors and acceptors, and relegated free oxygen to the function of sweeping up the debris, thus permitting the biologically reversible processes to run to completion. Whether the organic food molecule has its energy content enhanced by the protoplasm[1] or is activated by enzymes,[2] the result is a degradation resulting aerobically in relatively simple end-products of low available energy, and anaerobically in more or less complex organic fragments of higher energy content than the aerobic products. The two considerations, the simpler fragmentation of organic molecules and the probable analogy between initial aerobic and anaerobic transformations, add interest to the study of anaerobic metabolism.

Literature on the biochemistry of anaerobic microorganisms deals primarily with protein and carbohydrate cultures; that is, with systems of great chemical complexity which involve enzymic selectivity of optical isomers. The anaerobic degradation of fatty acids is largely free from these complications, and was accordingly chosen for the present studies. Anaerobic bacteria, capable of decomposing fatty acids, are widely distributed in nature; they give almost stoichiometric yields of methane and carbon dioxide, in a medium composed otherwise only of inorganic salts.

Hoppe-Seyler[3] found that calcium acetate could be fermented by inoculation with river mud, the products being methane and carbon dioxide in a 1:1 ratio. Mazé[4] identified a sarcina in similar acetate cultures and found it to produce gas only when supplemented by either of two accompanying rod-forms, though the latter alone could not produce gas. Omelianski[6] recognized this sarcina in cultures fed with other lower fatty acids; for example, butyric salts gave a 5:3 ratio of methane to carbon dioxide. Söhngen[6] studied fatty acid decomposition by cultures containing a sarcina

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[1] Mathews, in Cowdry's "General Cytology," 1924.

[2] Quastel, *Biochem. J.*, 20, 166 (1926).

[3] Hoppe-Seyler, *Z. physiol. Chem.*, 9, 561 (1887).

[4] Mazé, *Compt. rend.*, 137, 887 (1903); *Compt. rend. soc. biol.*, *398* (1915).

[5] Omelianski, *Centr. Bakt. Parasitenk.*, Abt. II, 15, 673 (1905).

[6] Sohngen, "Proefschrift," Delft, 1906; *Rec. trav. chim.*, 29, 238 (1910).

and a rod-form, these cultures being built up from canal or sewer slime by repeated treatment and decantation with a medium composed of 2% of calcium acetate in tap water to which 0.05% each of sodium chloride and dipotassium hydrogen phosphate had been added. Cultures active for most lower fatty acids were soon obtained and easily maintained, the organisms being lime-encrusted and predominantly in the sediment. Sohngen reports the following methane to carbon dioxide ratios: formate, 1:3; acetate, 2:2; butyrate, 5:3; caproate, 8:4; caprylate, 11:5; caprate, 14:6. Propionic, valeric, heptylic and nonylic acids failed to ferment. Coolhaas[7] has similarly studied formate and acetate fermentation by a thermophilic rod, obtaining ratios of 1:2 for formate and 2:2 for acetate.

In all of these investigations, one mole of carbon dioxide is assumed to remain in the sediment as calcium carbonate, the equations being written, for example, $Ca(C_2H_3O_2)_2 = 2CH_4 + CO_2 + CaCO_3$; a quantitative balance was possible, therefore, only in terms of methane, and the important transformations in combined oxygen had to be assumed. We have extended these experiments to include a complete balance of the participating substances, and in addition have collected some data on fatty acids with an uneven number of carbon atoms.

Experimental

Active Sohngen cultures were obtained from an actively fermenting sewage-sludge digestion tank. In preliminary experiments, 5 to 10 g. of the acid under investigation, as the sodium or calcium salt, was used in I-liter quantities of medium, the gas being collected over saturated brine and analyzed in an Illinois gas apparatus for carbon dioxide, hydrogen and methane. Since the inoculating organic matter equaled 50 to 75% of the fatty acid decomposed, controls on the inoculum alone were deducted from the final gas data. However, even controls, supplemented by analytical determinations of initial and final organic solids, do not completely guard against misleading gas ratios, and subsequent experiments have been, and are being, conducted in 8-liter reaction vessels, equipped for gas collection, to which several hundred grams of fatty acid can be fed. To avoid lethal osmotic effects and hydroxyl-ion concentrations, either the calcium salt, or the sodium salt plus some free acid, is fed in daily rations in the form of Sohngen medium, the displaced supernatant liquor being saved for analysis. Twenty-five to 50 g. of acid per week can be metabolized in such an apparatus, and the experiment continued until the organic matter in the initial inoculum is a negligible percentage of the total metabolism. Much of the carbon dioxide remains in the reaction vessel as carbonate or bicarbonate, the evolved gas showing about 30% of carbon dioxide, 65% of methane and small amounts of hydrogen and nitrogen. To the gaseous carbon

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[7] Coolhaas, *Centr. Bakt. Parasitenk*, Abt. II, *75*, 161 (1928).

dioxide must be added the final dissolved and combined carbon dioxide in the medium after deducting that determined initially in the reaction mix-

TABLE I

ANAEROBIC FERMENTATION OF SODIUM PROPIONATE

		G. 6.71 of sodium propionate	Control on inoculum alone, g.
Total gas evolved	CH_4	2.177	0.533
	CO_2	1.333	0.553
	H_2	0.009	0.002
Carbon dioxide in medium	Initial	1.26	1.28
	Final	4.12	1.45
Increase added to gas		2.86	0.17
Propionic acid	In inoculum	0.46	0.47
	Added	4.40	0.00
	Sum	4.86	0.47
	Recovered at end	0.21	0.11
	Propionic metabolized	4.65	0.36
Organic solids in inoculum	Initial	5.18	5.28
	Final	4.89	3.77

Theoretical CH_4 from 4.65 g. of acid = 1.76 g.
CH_4 found (2 177−0.533) = 1.644 g.; yield = 93.4%
Theoretical CO_2 = 3.45 g.
CO_2 found (1 333 + 2 86) − (0 553 + 0 17) = 3.470 g.; yield = 101.0%
Volume ratio, CH_4:CO_2 = 7:5.3.

TABLE II

ANAEROBIC FERMENTATION OF CALCIUM ACETATE (RESULTS IN GRAMS)

Added	Acetic acid	CH_4	CO_2	Total organic matter	Calcium as Ca	Phosphate as P_2O_5	Nitrogen as N
Initial inoculum	Trace	...	3.07	37.8	3.52	1.284	4.04
As Ca acetate	159.69	...	...	159.7	42.49	...	..
As tap water	...	...	0.68	...	0.29	...	0.01
As K_2HPO_4	...	...	...	...	...	1.753	..
Total	159.69	...	3.75	197.5	46.30	3.037	4.05
Recovered							
In reaction vessel	38.27	...	37.51	80.5	41.36	2.819	2.55
In displaced liquor	7.24	..	12.64	14.9	5.81	0.216	1.92
In gas	...	28.08	32.81	107.4	...	...	..
Total	45.51	28.08	82.96	202.8	47.17	3.035	4.47

Summary	Acetic metabolized	114.18 g.	
	Theoretical CH_4	30.489 g.	
	CH_4 produced	28.08 g.;	yield, 92.9%
	Theoretical CO_2	83.691 g.	
	CO_2 produced	79.22 g.;	yield, 94.7%
	Hydrogen produced	0.106 g.	
	Volume ratio, CH_4:CO_2 = 1:1.03		

TABLE III

ANAEROBIC FERMENTATION OF SODIUM PROPIONATE (RESULTS IN GRAMS)

Added	Propionic acid	Total solids	Organic matter
Initial inoculum	0.00	53.06	45.07
As sodium propionate	115.20	151.04	....
As propionic acid	53.28	53.28	168.48
As tap water	....	1.51	....
As inorganic salts	....	6.96	....
Total	168.48	265.85	213.55
Recovered			
In reaction vessel	38.42	110.64	80.96
In displaced liquor		32.90	11.84
In gas	....	145.15	145.15
Total	38.42	288.69	237.95
Correction for H_2O reacting		21.90	15.82
Corrected solids		266.79	222.13

Summary	Propionic acid metabolized	130.06	
	CH_4 produced	48.587;	yield, 98.7%
	CO_2 produced	96.320;	yield, 99.6%
	H_2 produced	0.243	
	Volume ratio, $CH_4:CO_2$ =	7:5.05	

TABLE IV

SUMMARY OF $CH_4:CO_2$ RATIOS FOR FATTY ACID FERMENTATIONS

Fatty acid	Number of detns.	Average H_4 : C02 ratio found	Theoretical ratio (see below)
Acetic	2	1:0.97	1:1
Propionic	8	7:5.04	7:5
n-Butyric	3^a	5:2.7	5:3
n-Valeric	1^a	13:6.7	13:7
Oleic	1^a	25:12.0	...
Lactic	1"	1:1.06	...

[a] Preliminary data; these data are being extended to more precise determinations particularly of the anabolic phase of the process.

ture and that added as tap water in the daily rations of Sohngen medium. Olefins, carbon monoxide or higher homologs of the methane series were not present in determinable amounts, because the methane analytically determined in the combustion pipet checked the carbon dioxide produced in the combustion. Table I illustrates the more essential points in the preliminary tests with 1-liter cultures and Table II those with 8-liter daily feeding experiments. In the latter case, calcium, phosphate and nitrogen balances are included to indicate the magnitude of sampling errors. Table III gives the results of a propionate feeding experiment. A summary of results in terms of $CH_4:CO_2$ ratios is shown in Table IV.

Oleic and lactic acids are included merely for comparison; these types are reserved for future consideration when the saturated normal and branched-chain acids have been fully studied.

Discussion of Results

The lower fatty acids are characterized by (1) a high yield of methane from the acid metabolized; (2) a much larger yield of carbon dioxide than can be contributed by simple decarboxylation (except acetic); and **(3)** traces of hydrogen in the gas evolved. Of the fatty acid metabolized, 90 to 95% appears as gas; the remainder presumably is consumed in anabolism through intermediary production of amino acids, because the simultaneous feeding of amino acid (glycocoll) temporarily stops gas production.

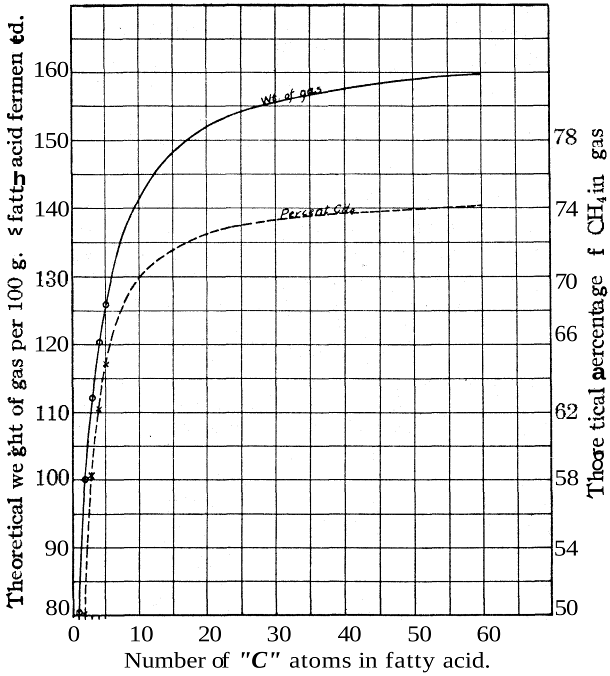

Fig. 1.—Theoretical weight and methane content of fermentation gases.

With the exception of acetic acid, the respiratory degradation yields carbon dioxide in excess of the carboxyl group; changes in the weight of organic inoculum are negligible, phosphates are not reduced, sulfates are absent from this tap water, and the total nitrate and dissolved oxygen introduced in the daily ration represent quantitatively only a fraction of a gram of carbon dioxide. The additional oxygen, therefore, must come from water, and the number of molecules of water needed to balance equations expressing the observed gas ratios is found to increase regularly with the length of the carbon chain, and to be expressed by the simple relation: moles of water required per mole of acid $= (n - 2)/2$, where n is the number of carbon atoms in the acid. Thus the general equation is

$$C_nH_{2n}O_2 + \frac{(n-2)}{2} H_2O = \frac{(n+2)}{4} CO_2 + \frac{(3n-2)}{4} CH_4$$

or for propionic acid it is

$$4C_3H_6O_2 + 2H_2O = 5CO_2 + 7CH_4$$

While ascending the homologous series, above acetic, therefore, the weight of gaseous products exceeds the weight of acid (as shown in Fig. 1) by an increasing percentage, attaining a purely hypothetical maximum of 164% of the acid decomposed for an infinite number of carbon atoms. The percentage of methane in the gaseous products also increases to a hypothetical limit of 75% by volume, although, due to the solubility and chemical retention of carbon dioxide in the medium, the evolved gases often contain 80 to 85% of methane.

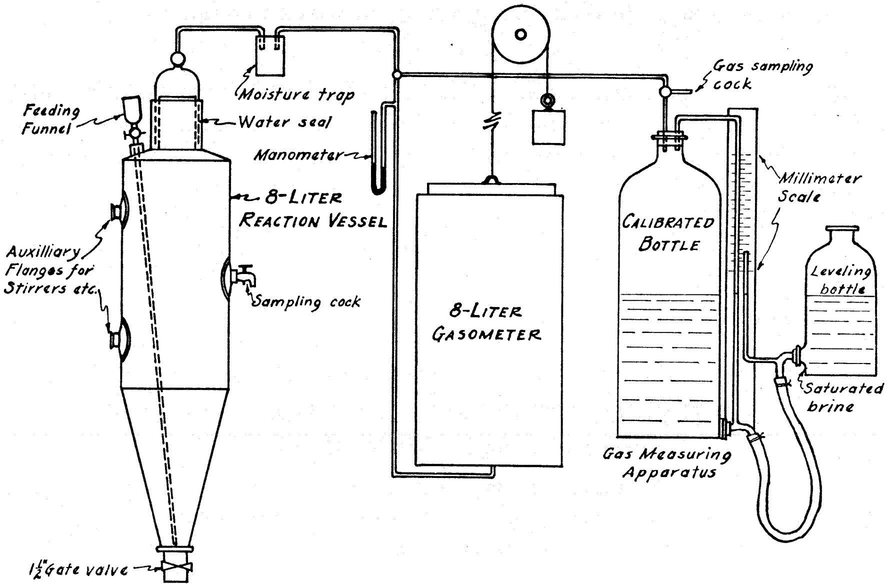

Fig. 2.—Apparatus for anaerobic metabolism studies.

The intermediate steps in this oxidation by water are yet to be revealed, but they are evidently not hydrolysis. The feeding of sodium propionate, for example, involves hydrolysis to liberate the free acid and due allowance must be made for this in analytically balancing the reactants, but the utilization of half a molecule of water by each molecule of propionic acid involves not simple hydroxylation but carboxylation of one of the carbon atoms; it is a process of intermolecular oxidation and reduction.

Most of our fermentation tests have shown the production of slightly more carbon dioxide than is predicted by the above respiratory mechanism. No extra-cellular side reactions have been detected to explain the excess of carbon dioxide and the evolution of hydrogen; accordingly, both of these substances are regarded as clues to the anabolic processes, and the following three types of reactions are being investigated: (a) $CHEOOH + 2H_2O = 2CO_2 + 4H_2$; (b) $RCH_2COOH + NH_3 = RCH(NH_2)COOH + H_2$; (c) the production of higher homologs, such as the formation of succinic from acetic, which Quaste1[2] mentions, followed by decarboxylation to propionic acid. The experimental evidence favors the first two reactions, operating probably in the form of a cycle with hydroxy acid, then amino acid production representing the anabolic phase, as in the animal body;[8] the reverse process, including oxidation by water, would be the catabolic phase. The production of hydroxy and amino acids would yield hydrogen, and the catabolic oxidation would explain the excess carbon dioxide observed in these experiments. Such a cycle has the added interest of involving alpha, and not beta, oxidation of the carbon chain.

Summary

1. A study has been made of the anaerobic breakdown of lower fatty acids by microorganisms converting them into methane and carbon dioxide.
2. Water has been shown to act as an oxidizing agent in this degradation, and a simple relation to exist between the number of carbon atoms in the acid and the number of participating water molecules.
3. Concurrent side reactions are demonstrated and their probable mechanisms discussed.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATIOM OF MERCURY DIALKYLS FROM ORGANOMAGNESIUM HALIDES

BY HENRY GILMAN AND ROBERT E. BROWN

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Introduction

Some improvements were described recently[1] for the preparation of mercury dialkyls from mercuric chloride and the Grignard reagent. This is one of the best methods for the synthesis of this class of compounds. The improvements suggested then were: first, the use of a Soxhlet extractor to facilitate manipulation of the mercuric halide; second, the use of a larger volume of ether to reduce caking; and, third, a marked extension in the time of heating.

In those experiments a liberal excess of Grignard reagent was used. We have now shown that it is possible to synthesize some typical mercury dialkyls with practically an equivalent quantity of organomagnesium

[8] Knopp, Science, 71, 23 (1930).

[1] Gilman and Brown, THIS JOURNAL, 51, 928 (1929). This article contains references to earlier studies, particularly those of Marvel and co-workers.

halide. Furthermore, the time required to obtain essentially equal (and in some cases markedly superior) yields can be drastically reduced.[2] These two improvements probably make this reaction the best now available for the preparation of mercury dialkyls on a laboratory scale.

Experimental Part

The appropriate Grignard reagent was decanted from unused magnesium into a two-liter, three-necked flask provided with a mercury-sealed mechanical stirrer and a Soxhlet extractor holding a water-condenser.' Dry ether was added to the reaction flask until its contents were 800 cc., and one-half mole of mercuric chloride[3] was placed in the extraction thimble. The flask was heated until the ether boiled gently, and when all of the mercuric chloride had been added to the Grignard reagent,[4] the extractor was replaced by a long condenser set for distillation. The water in the bath surrounding the reaction flask was slowly brought to boiling,[5] and then maintained at this temperature for one hour. Stirring was continued during the entire distillation and heating.

The water-bath was then cooled, and after returning the ether distillate to the reection flask,[6] hydrolysis was effected with water or with an ammonium chloride solution containing a small quantity of ammonium hydroxide. The ether layer was separated and combined with two 25-cc. portions of ether which were used to wash the water layer. The combined ether solutions were dried over calcium chloride (about 10 g.) and then distilled through an efficient column.[1]

The troublesome, readily volatile butylmercuric halides were easily and almost completely removed by freezing them out (by ice and water cooling) from the mercury di-n-butyl after the ether was removed. This treatment is unnecessary with the methyl- and ethylmercuric halides because of their much lower volatility.

One experiment was carried out for the preparation of mercury diphenyl by a slight modification of the method just described. Because of the low solubility of aryl mercury compounds in ether, 500 cc. of benzene and 300 cc. of ether were added to the phenylmagnesium bromide prior to the introduction of mercuric chloride. The mercury diphenyl was extracted from the reaction mixture with chloroform, and twice recrystallized from this solvent. The yield of mercury diphenyl was 70.6% from 1.15 moles of phenylmagnesium bromide and 0.5 mole of mercuric chloride.

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[2] The improved yields reported in our first paper (Ref. 1) in which the time of heating was extended beyond that used by earlier investigators led us to believe that the yields then reported might have been increased significantly by a more protracted period of refluxing. From the present results it appears that the time might be reduced to an even greater extent if it were possible to add the mercuric chloride in solution more rapidly.

[3] The mercuric chloride was dried in a desiccator for these experiments. In the previous study (Ref. 1) the mercuric halide was used directly from a stock bottle. This added precaution of drying may be unnecessary.

[4] This required about four hours with the Soxhlet extractor used by us. When the experiment is carried out during winter or in a cool room, it is advisable to wrap a towel around the extractor to prevent separation of mercuric chloride in the small turn of the extractor.

[5] During this time practically all of the ether was removed by distillation.

[6] The ether distillate was returned to the flask in order to moderate, where necessary, the vigor of subsequent hydrolysis. Also, this serves to assemble any small quantity of lower molecular weight mercury dialkyl which might have been carried over with the ether.

The results are summarized in Table I and the footnotes which accompany it.

TABLE I

MERCURY DIALKYLS

Grignard reagent	Moles	Mercuric chloride, mole	% Yield of mercury dialkyl
CH_3MgI	1.2[a]	0.5	71.2
CH_3MgI	1.15	.5	70.2
C_2H_5MgI	1.15	.5	82.0, 80.4 and 84.4[b]
n-C_4H_9MgBr	1.15	.5	80.1 and 80.0[c]

[a] The number of moles of each Grignard reagent refers to the quantity of halide used, and not the actual quantity of RMgX compound available. When allowance is made for the small loss incidental to decantation from unused magnesium, and, more particularly, to the actual yields of Grignard reagents from a given weight of RX compound [see Gilman, Zoellner and Dickey, THIS JOURNAL, 51, 1576 (1929)] it is altogether possible that we may not have had the required one mole of Grignard reagent. In order to be more certain on this point, an experiment was carried out with 1.1 mole of ethylmagnesium iodide and 0.5 mole of mercuric chloride. Here the Grignard reagent was estimated quantitatively by our titration method. The yield in this preparation was the 84.4% reported in Table I, and a positive color test[7] at the end of the reaction showed an excess of ethylmagnesium iodide.

[b] The yield of mercury diethyl obtained previously (Ref. 1) by us was about 88%.

[c] The maximum yield of mercury di-n-butyl reported previously by us was 66.7%.

Miscellaneous Observations.—In connection with interpretations of the reaction, mercury-diethyl, -di-*n*-butyl and -diphenyl were each treated with magnesium bromide and magnesium iodide, respectively. However, in no case (under our experimental conditions) was there a positive color test[7] to indicate the formation, in appreciable quantities, of an RMgX compound. Incidental to these studies, a highly interesting observation was made: namely, a few drops of mercury diethyl were sufficient to induce complete solution of a relatively large quantity of magnesium iodide-etherate in ether.

The stability of mercury dialkyls and diaryls varies greatly. Mercury dimethyl showed no signs of decomposition after five months' standing in a pyrex flask closed with a cork. Both mercury diethyl and mercury di-n-butyl showed signs of decomposition; *i.e.*, deposition of a gray film of metallic mercury, within a few days even in glass-stoppered, brown bottles. Solid pure mercury diphenyl appears to remain white indefinitely; however, even a slightly impure product turns yellow on standing.

The well-known physiologically deleterious properties of mercury dialkyls and diaryls were frequently noticed. Mercury dimethyl appeared to be the most objectional to work with, in part, because of its high vapor pressure at room temperature. The odor of mercury diphenyl is very per-

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[7] Gilman, Sweeney and Heck, THIS JOURNAL, 52, 1604 (1930). This article contains references to earlier studies on the sensitive color test for reactive organometallic compounds.

sistent, and this disagreeable odor becomes more acute with continued exposure to the compound or its vapors. Some individuals appear to have an idiosyncrasy toward the vapor of organic mercurials, and are distinctly more affected than others.

Summary

Some improvements in the preparation of mercury dialkyls from mercuric chloride and the Grignard reagent make this synthesis the best for such compounds on a laboratory scale.

Miscellaneous observations have been reported on the stability, physiological action and behavior toward magnesium halides of mercury dialkyls and mercury diphenyl.

AMES, IOWA

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SHARP AND DOHME]

AMINO-ALCOHOLS. II. HOMOLOGS AND ANALOGS OF PHENYLPROPANOLAMINE

BY WALTER H. HARTUNG, JAMES C. MUNCH, W. ALLAN DECKERT AND FRANK CROSSLEY

RECEIVED MAY 1, 1930 PUBLISHED AUGUST 5, 1930

The preparation of phenylpropanolamine and its *p*-methyl derivative by reduction of the corresponding oximino ketones has been described.[1] By employing the same technique, it has been possible to prepare other members of the arylalkanolamine series from phenylethanolamine to phenyloctanolamine. Diphenylethanolamine was prepared by the catalytic reduction of benzoin oxime, both the *a*- and β-oximes yielding the amino-alcohol melting at 165°.

Procedure

The higher intermediate oximino ketones were prepared according to the method already described for isonitrosopropiophenone and its #-methyl derivative, with uniformly good results, although the longer the alkyl side chain, the poorer the yields of purified isonitroso ketone. The lower yields are probably caused by complications attending isolation of the product rather than by incomplete nitrosation, for in no case was it possible to recover unchanged ketone.

Isonitroso-acetophenone was best obtained according to the directions of Claisen and Manasse[2] by allowing butyl nitrite and acetophenone to react in an absolute alcoholic solution containing sodium ethoxide. The method which gave such excellent results with propiophenone and its higher homologs gave very poor yields with acetophenone—6 to 12%.

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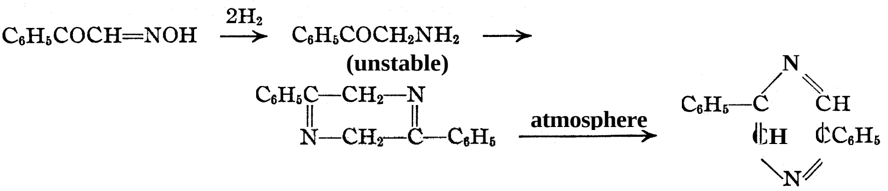
[1] Hartung and Munch, THIS JOURNAL, 51, 2262 (1929).

[2] Claisen and Manasse, *Ber.*, 20, 2194 (1887).

Alpha- and β-benzoin oximes were prepared and separated according to the directions of Werner and Detscheff.[3]

The conversion of the oximino ketones, by means of palladium, into the corresponding amino-alcohols by hydrogenation in absolute alcoholic solution containing three equivalents of hydrogen chloride has already been described in connection with the preparation of phenylpropanolamine.[1] This process served equally well for the reduction of the higher homologs and of the benzoin oximes. The products were obtained as their hydrochlorides, from which the free bases could be isolated. The yields were good.

Isonitroso-acetophenone, however, was not so readily reduced to phenylethanolamine, for in only one instance was it possible to go directly from oximino ketone to amino-alcohol; in all other attempts the reduction stopped at the amino ketone stage; this intermediate product was then isolated as hydrochloride and further reduced in aqueous solution by means of fresh catalyst to the desired amino alcohol. When isonitroso-acetophenone was reduced in the absence of hydrogen chloride a product was obtained which after removal of the catalyst and allowing the alcoholic filtrate to stand exposed to the atmosphere melted at 195–196° and corresponded with the diphenylpyrazine described by Braun and Meyer.[4] The formation of this compound may readily be accounted for in the following manner



for Gabriel[5] has pointed out how free amino ketones spontaneously form dihydropyrazines and how readily these are in turn oxidized to the stable pyrazine derivatives.

Pharmacological

All of these compounds are of physiological interest by virtue of their relation to ephedrine and ephedrine-like substances. In the first paper it was pointed out that the pharmacodynamic activity of primary amino-alcohols of the type $ArCHOHCHRNH_2$ merited a more detailed study, and since then Chen and his co-workers,[6] have justified this prediction by showing that primary amino derivatives of the sympathomimetic type are, in general, more potent as pressors than the corresponding methylamino

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[3] Werner and Detscheff, Ber., 38, 72 (1905).

[4] Braun and Meyer, *ibid.*, 21, 19 and 1269 (1888).

[5] Gabriel, *ibid.*, 41, 1143 (1908).

[6] Chen, Wu and Henriksen, J. *Pharmacol.*, 36, 363 (1929).

derivatives; thus Chen[7] points out that dl-phenylpropanolamine is a stronger pressor than dl-phenylpropanol-methylamine (dl-ephedrine). Our present interest in compounds of the ephedrine and adrenaline type has been centered chiefly on the primary rather than on the methylated amines.

The compounds prepared and studied are given in Table I. Since a more complete pharmacological report will be published elsewhere, a brief review of the hypertensive properties will suffice here. Phenylethanolamine (I) has already been somewhat extensively investigated.[8] The physiological action of phenylpropanolamine and its p-methyl derivative (II and III) has already been described;[1,9] a correction should, however, be made as to the pressor activity of *p*-tolylpropanolamine, which has been found since our previous paper to be about three-fifths as active as phenylpropanolamine. Phenylbutanolamine (IV) has been investigated by Chen, Wu and Henriksen,[6] and found to possess comparatively very low activity on decerebrate cats, which observation has been confirmed by our results on anesthetized dogs. Phenylhexanolamine hydrochloride (VII) administered intravenously to an anesthetized dog in doses of 10 mg./kg. caused a marked fall in blood pressure, that persisted for about thirty minutes and was followed by a gradual rise which after several hours reached a new level as much above as the fall was below normal. The remaining members of the series show no pressor effect within the range of doses thus far tried.

TABLE I

PHARMACOLOGICAL DATA

	Amino-alcohol $ArCHOHCH(NH_2)R$ At	R =	Minimum lethal dose of hydrochloride, mg./kg. Subcutaneous to guinea pigs	Intravenous to rabbits
I	C_6H_5	H	1000	90[b]
II[a]	C_6H_5	CH_3	600	75
III[a]	$C_6H_4Me(p)$	CH_3	175	33
IV	C_6H_5	C_2H_5	250	60
V	$C_6H_4Me(p)$	C_2H_5	150	25
VI	C_6H_5	$C_3H_7(n)$	300	40
VII	C_6H_5	$C_4H_9(n)$	250	20
VIII	C_6H_5	$C_6H_{13}(n)$	450	10
IX	C_6H_5	C_6H_5	450	60

[a] Repeated for comparison. [b] Alles, J. *Pharmacol.*, 32, *121* (1927), gives this dose as 30 mg./kg.

From these results it appears that pressor activity is associated with compounds having the general formula ArCHOHCHRNH—, but this activity is exerted at its best when the side chain contains two or three carbons.

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[7] Chen, Ref. 6, p. 394.

[8] Cf. Gordon, *J. Am. Pharm.* Assn., *17*, 1195 (1928), and bibliography; Tainter, *J. Pharmacol.*, 36, 29 (1929).

[9] See also Chen, *ibid.*, 36,394 (1929).

If to phenylpropanolamine (II) a methyl is added to the amino group (ephedrine) or to the aromatic nucleus (111), its pressor activity is modified but not destroyed, whereas by adding the methyl to the end of the side chain (IV), this potency has been so diminished as practically to be eliminated. The peculiar behavior of phenylhexanolamine is being further investigated.

Considering the series as a whole, the most striking fact is the ability of the organism to respond so readily and characteristically to what the chemist may ordinarily consider as correspondingly minor changes. All the members of this series contain substantially the same chemically active groupings and give essentially the same type of reactions, yet the organism is capable of responding readily to a change in molecular structure which could, by purely chemical means, be substantiated only with the greatest effort and difficulty. The explanation for such selectivity on the part of an organism in a series of this kind would be most desirable and an invaluable contribution to our present limited and confused knowledge of the relationship between physiological activity and chemical structure.

A survey of the toxicities reveals no parallelism between the two methods of determination. There is, however, a remarkable regularity of increase in the toxicity on intravenous administration of the phenylalkanolamines with increase in length of the side chain. Another striking fact is the much greater toxicity of the *p*-tolyl derivatives (III and V) as compared with the corresponding phenyl products (II and IV), which lends support to the observation of de Burnaga Sanchez[10] that *p*-methylephedrine is about 20% more toxic than ephedrine.

Experimental

The ketones were all prepared by the Friedel–Crafts reaction from the appropriate acid chloride and benzene or, in the case of the tolyl ketones, toluene. All, with one exception, are described in Beilstein.

Octanophenone (phenyl heptyl ketone) is a liquid, having an odor characteristic of the series, which boils at 140–145° (5 mm.) or 150–153" (7 mm.); it forms a semicarbazone which may be recrystallized from benzene–ligroin mixture and melts at 125.0–125.5".

The isonitroso ketones, with analyses, are given in Table II.

TABLE II

ISONITROSOKETONES

Oximino ketone	Yield. %	M. p.. °C.	Nitrogen, % Found (Kjeldahl) I	II	Calcd.
Isonitrosobutyrophenone[a]	50	49	8.03	7.98	7.91
p-Methylisonitrosobutyrophenone	50	78	7.53	7.56	7.33
Isonitrosopentanophenone	69	69	7.49	....	7.33
Isonitrosohexanophenone	55–60	53–54	7.07	7.05	6.83
Isonitroso-octanophenone	25	38.5	5.88	5.83	6.0

[a] This compound was isolated but not purified by Müller and v. Pechmann, *Ber.*, 22, 2131 (1889).

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[10] De Burnaga Sanchez, Bull. *soc. chim.*, [4] **45**, 284 (1929).

Table III contains a summary of the data obtained on the amino-alcohols.

TABLE III

AMINO-ALCOHOLS

No.	Amino-alcohol	M. p., °C.	Nitrogen, % Found (Kjeldahl)		Nitrogen, % Calcd.
1	Phenylbutanolamine[a]	80.5–81.0	..	..	..
2	*p*-Tolylbutanolamine	85.0	7.77	7.89	7.82
3	Phenylpentanolamine[a]	70–71	..	..	..
4	Phenylhexanolamine[a]	72.0–72.5	..	..	..
5	Phenyloctanolamine[b]	79	..	..	..

HYDROCHLORIDE

No.	M. p., °C.	Chlorine, % Found, (AgCl) I	Chlorine, % Found, (AgCl) II	Chlorine, % Calcd.
1	242	17.59	17.60	17.59
2	255	16.32	16.42	16.47
3	222	16.56	16.76	16.47
4	197.5–198.0	15.61	...	15.54
5	157.5	13.77	13.45	13.79

[a] These products were prepared by Tiffeneau and Lévy [*Bull. soc. chim.*, [4] 37, 1247 (1925); *Compt. rend.*, **183**, 969 (1926)], according to the method

$$C_6H_5CHOHCN \text{ (or } C_6H_5CHOHCONH_2) \xrightarrow{RMgX} C_6H_5CHOHCOR \xrightarrow{H_2NOH}$$

$$C_6H_5CHOHCR{=}NOH \xrightarrow{H_2} C_6H_5CHOHCHRNH_2$$

and they give the following melting points: phenylbutanolamine, 76–78'; phenylpentanolamine, 70–72°; phenylhexanolamine, 65–66°. They did not describe the hydrochlorides. [b] Phenylheptanolamine was prepared but not analyzed; the following information is appended for reference and convenience. Isonitrosoheptanophenone, m. p. 33°; phenylheptanolamine base, m. p. 62.5°, hydrochloride, m. p. 181.0–181.5°.

Diphenylethanolamine may be prepared from benzoin oxime by means of sodium and absolute alcohol[11]' but that method gives relatively low yields and the product contains some isodiphenylethanolamine. The catalytic reduction of both α- and β-benzoin oximes gave quantitative yields of pure diphenylethanolamine, isolated as hydrochloride, the salt melting at 235°, and the base at 165°.[12]

Summary

1. The reduction of oximino ketones to the corresponding amino-alcohols by catalytic means has been extended.

2. It has been shown that in this series pressor activity is associated with compounds having the general formula $ArCHOHCHRNH_2$, but that this activity is more intimately connected with ethane and propane derivatives.

3. Phenylhexanolamine caused a fall in blood pressure that was followed by a gradual rise which after several hours reached above normal.

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[11] Polonowski, *Ber.*, **21**, 488 (1888).

[12] Cf. Beilstein, 3d ed., Vol. II, p. 1078.

4. The toxicities, as determined by intravenous injection to rabbits, show a regular increase as the length of the side chain increases.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

THE ACTION OF THE HALOGEN HYDRINS AND OF ETHYLENE OXIDE ON THE THIOUREAS

BY JOHN F. OLIN AND F. B. DAINS

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The basis of this investigation was the observation that thiocarbanilide could be desulfurized with ethylene chlorohydrin, as follows. The thiourea was boiled with the chlorohydrin, giving a partial yield of diphenylurea which could be increased to 60% by heating the reaction product with alcoholic potassium hydroxide, thus completing the hydrolysis of the intermediate thio ether, $C_6H_5NHC(NC_6H_5)SCH_2CH_2OH$.

In order to throw more light on these results, which are analogous to the desulfurizing effect of chloro-acetic acid, the action of the chlorohydrins on thioureas and mono- and disubstituted thioureas was studied.

The results show that the primary product is a thio ether which can be isolated in many cases as the halogen hydride salt. These thio ethers are hydrolyzed with great ease, yielding a mixture of decomposition products.

When the hydroxyl of the hydrin is replaced by an ether or ester grouping, the compound is more stable. In the unsubstituted γ-thio ethers the NH and NH_2 groups react readily with acyl chlorides, yielding diacyl derivatives of the type $RCONHC(NCOR)CH_2CH_2OH(R)$, and with phenyl isocyanate, ethers of thiocarbonyl-diurea, $(R)HOCH_2CH_2SCNHCONHC_6H_5(NCONHC_6H_5)$.

Ethylene oxide was found to add to the C–SH groups, giving ethers, $RNHC(NR)SCH_2CH_2OH$, which in the case of thiocarbanilide could be isolated; in other instances only the hydrolysis products were identified.

Experimental

Ethylene Chlorohydrin and Thiourea. Oxyethylthiourea Hydrochloride, $HOCH_2CH_2SC(NH)NH_2$.—When the molar mixture is heated for thirty minutes, allowing the temperature to rise slowly from 90 to 105° and no higher, no precipitation of ammonium chloride occurs. The resulting product is a heavy oil soluble in alcohol and acetone but not in other organic solvents. Cold dry ether precipitated the hydrochloride which crystallized from butyl alcohol in slender needles melting at 111° and which probably had been obtained by Schatzmann,[1] though no melting point was given

Anal. Calcd. for $C_3H_8N_2OSHCl$: N, 17.90. Found: N, 17.87.

All efforts to close the ring, thus forming the simple thiazolidine $\underline{SC(NH)NHCH_2CH_2}$

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[1] Schatzmann, Ann., 261, 1 (1891).

have thus far failed. In the case of the substituted amino-ethanol-thiourea, with the grouping $N—CH_2CH_2OH$, ring closure with the enol SH group is easily effected.2

Ethylene bromo- and iodohydrins show the same general behavior as the chlorohydrins, but give oily non-crystallizable products.

When the reaction temperature of the mixture is allowed to rise to 135–140°, precipitation of ammonium chloride occurs, the weight of which amounts to about one fourth of the total nitrogen, and the residue consists of a mixture of unidentified compounds consisting in part of polymers of thio-ethyleneglycol.

Trimethylene Chlorohydrin and Thiourea. Oxypropylthiourea Hydrochloride, $H_2NC(NH)CH_2CH_2CH_2OH.HCl$.—When molar quantities of the two reagents are heated carefully at 120–125°, an oil is formed which solidifies when treated with dry ether. The crystals from butyl alcohol melt at 130°.

Anal. Calcd. for $C_4H_{10}N_2OS{\cdot}HCl$: N, 16.43. Found: N, 16.25.

Repeated evaporation of the thiourea with ammonium hydroxide gave guanidine, identified as its nitrate (m. p. 209°) and its dibenzoyl derivative (m. p. 214°).[3] Ethylamine yielded ethylguanidine, the dibenzoyl derivative of which melts at 87".

Anal. Calcd. for $C_{17}H_{17}N_3O_2$: N, 14.24. Found: N, 14.19.

Methylguanidine was formed in like manner from the thio ether and methylamine.

p-Bromo-ethyl Ether and Thiourea. γ-Ethoxyethylthiourea Hydrobromide, $NH_2C(NH)SCH_2CH_2OC_2H_5{\cdot}HBr$.—The components diluted with a little alcohol were heated for thirty minutes at 100°. After removal of the excess bromo ether and alcohol by vacuum distillation, the hydrobromide salt melting at 28–29" was isolated. The oily free base is unstable.

Anal. Calcd. for $C_5H_{12}N_2OS{\cdot}HBr$: N, 12.23. Found: N, 12.33.

Heating the thiourea ether with potassium hydroxide gave the strong smelling ethoxyethyl mercaptan (b. p. 125–126° at 740 mm.).[4]

Thioncarbanilic p-Ethoxyethyl Ester, $C_6H_5NHCOSC_2H_4OC_2H_5$.—To further characterize the mermptan, it was heated in a bomb tube for four hours at 150° with phenyl isocyanate. The resulting oily ester slowly crystallized in plates melting at 45°.

Anal. Calcd. for $C_{11}H_{15}NO_2S$: N, 6.22. Found: N, 6.17.

Its isomer, thiolcarbanilic β-ethoxyethyl ester, is formed when phenyl mustard oil is heated with the monoethyl ether of ethylene glycol at 150°.

Anal. Calcd. for $C_{11}H_{15}NO_2S$: N, 6.22. Found: N, 6.35.

It melts at 42–43°, but a mixture of the thiol and thion esters liquefies at room temperature. This ester was converted into its thiol isomer by heating with ethoxyethyl iodide at 130° for four hours.[5] The resulting product melted at 44°. Its constitution was proved by a mixed melting point with the thiol ester, by its dissociation into phenyl isocyanate and mercaptan at 150° and by the formation of carbanilide and mercaptan when heated with aniline.

Phenyl isocyanate adds to the NH and NH_2 groups giving with the above thiourea, the ethoxyethyl ether of thiocarbonyldiphenyl-diurea, $C_6H_5NHCONHC(NCONHC_6H_5)SC_2H_4OC_2H_5$. The hydrogen bromide salt of the thio ether (12 g.) in concentrated water solution was treated with phenyl isocyanate (12 g.) and potassium hydroxide (3 g.). The resulting heavy oil on crystallization from alcohol gave a solid melting at 132°.

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[2] Dains, Brewster, Blair and Thompson, THIS JOURNAL, 44, 2639 (1922).

[3] Korndorfer, *Archiv. Phar.*, 241,478 (1903).

[4] Rojahn and Lemme, *ibid.*, 263, 623 (1925). From potassium hydrosulfide and the bromo ether.

[5] Wheeler and Barnes, Am. *Chem.* J.,24, 71 (1902).

Anal. Calcd. for $C_{19}H_{22}N_4O_2S$: N, 14.52. Found: N, 14.39.

Its identity was proved by its conversion by means of alcoholic ammonia[6] into the diphenyl amide of guanidine dicarboxylic acid (m. p. 176°) and mercaptan. The corresponding methyl ether gives the same guanidine derivative? Phenyl isothiocyanate yields only oily addition products with the thio ethers.

p-Ethyl Acetate Derivative of Isothiourea, $CH_3COOCH_2CH_2SC(NH)NH_2HBr$.—$\beta$-Bromo-ethyl acetate heated at 125° formed an oil which crystallized from acetone in needles melting at 99°.

Anal. Calcd. for $C_5H_{10}N_2O_2S \cdot HBr$: N, 11.53; Br, 32.28. Found: N, 11.64; Br, **32.04.**

The ester heated with aniline gave phenylguanidine and with phenyl isocyanate a thiocarbonyl diurea derivative melting at 134°.

Anal. Calcd. for $C_{19}H_{20}N_4O_4S$: N, 14.01. Found: N, 13.80.

The acyl chlorides yield with the thiourea ethers α,β-diacyl derivatives of the type $RCONHC(NCOR)S—R'$. Thus acetyl oxyethyl isothiourea with benzoyl chloride gives a heavy oil, but with *p*-nitrobenzoyl chloride in pyridine solution, the di-p-nitrobenzoyl thiourea ether, melting at 189°, resulted.

Anal. Calcd. for $C_{19}H_{18}N_4O_8S$: N, 12.13. Found: N, 12.30.

The α,β-dibenzoyl-γ-methyl thiourea (m. p. 149°) is readily formed from benzoyl chloride and the methyl thiourea in alkaline solution.[8]

Anal. Calcd. for $C_{16}H_{14}O_2N_2S$: N, 9.40. Found: N, 9.53.

That it has the symmetrical constitution or rearranges easily to it is shown by the fact that on heating with aniline the known dibenzoyl-monophenylguanidine (m. p. 185°) was obtained and confirmed by a mixed melting point.[9]

Reactions with Monophenylthiourea. **γ-Hydroxyethyl-phenylthiourea Hydroiodide,** $C_6H_5NHC(NH)SC_2H_4OH$.—The iodohydrin and phenyl thiourea were heated in alcohol solution at water-bath temperature and the resulting heavy oil after washing with ether was dried at 100° *in vacuo.*

Anal. Calcd. for $C_9H_{13}N_2OS \cdot HI$: N, 8.62. Found: N, 8.49.

The free base is a heavy oil which rapidly decomposes, yielding mono-phenyl urea and mercaptan. Boiled with sodium hydrosulfide, the ether gives the phenyl thiourea. With ethylene chlorohydrin only decomposition products were obtained.

γ-Acetyl-oxyethyl-phenylthiourea, $C_6H_5NHC(NH)SCH_2CH_2OCOCH_3$, was isolated as the hydrogen bromide salt (m. p. 158°). The free is base fairly stable and melts at 69–70°.

Anal. Calcd. for $C_{11}H_{14}N_2O_2S$: N, 11.77. Found: N, 11.78.

Aniline at 150° gave diphenylguanidine (m. p. 146°).

Nitrobenzoyl chloride in pyridine solution formed an acyl derivative, crystallizing from alcohol in orange colored flakes melting at 132°.

Anal. Calcd. for $C_{18}H_{17}N_3O_5S$: N, 10.85. Found: N, 10.67.

Its stability would point to the symmetrical structure.[10] With phenyl isocyanate, it showed the usual behavior, yielding the thio ether of 1,5-diphenyl-4-monothiobiuret, $C_6H_5NHCONH(SC_2H_4OCOCH_3)NHC_6H_5$, m. p. 81–82°.

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[6] A convenient method for this type of reaction is to dissolve the substance in alcohol in a Dewar flask, add liquid ammonia and allow the solution to slowly evaporate.

[7] Lakra and Dains, THIS JOURNAL, 51, 2223 (1929).

[8] The corresponding dibenzoyl-y-ethyl thiourea melts at 112°.

[9] McKee, *Am. Chem. J.*, 26, 222 (1901); Kampf, *Ber.*, **37**, 1683 (1904).

[10] Wheeler, Am. *Chem.* J., 27, 279 (1902).

Anal. Calcd. for $C_{18}H_{19}N_3O_3S$: N, 11.70. Found: N, 11.63.

Disubstituted Thioureas. **Thiocarbanilide** and **β-Chloro-ethyl** Benzoate.—Molar proportions were heated alone or in xylene solution at 130–150° for several hours. From the reaction mixture were isolated diphenylurea, phenyl mustard oil, benzanilide, benzoic acid, sulfur containing oils and 2,3-diphenylthiazolidine (m. p. 136°).

Two sets of reactions evidently occur; first, the formation of a thio ether which is then hydrolyzed to the urea, benzoic acid, and mercaptan; second, dissociation of the thiocarbanilide into phenyl isothiocyanate and aniline, which with the chloro-ethyl benzoate gives phenylamino-ethanol benzoate. The amino-ethanol adds the mustard oil, yielding the thiourea. The thiazolidine results from loss of benzoic acid, closing the ring.[11] The possibility of such a reaction is shown experimentally as follows.

β-Phenylamino-ethyl benzoate (m. p. 78") gave with phenyl isothiocyanate in alcohol solution the benzoate of γ,β-diphenyl-γ-ethanol thiourea, $C_6H_5NHCSN(C_6H_5)CH_2CH_2O—COC_6H_5$, melting at 145°.

Anal. Calcd. for $C_{22}H_{20}N_2O_2S$: N, 7.45. Pound: N, 7.61.

The ring is closed when the thiourea is heated with hydrochloric acid, yielding the 2,3-diphenylthiazolidine and benzoic acid. Since no evidence of ring formation has been obtained from the hydroxy-ethyl thio ethers, the above seems the most probable explanation of the reaction. Thiocarbanilide and mono-m-nitrodiphenylthiourea formed the usual y-thio ethers with bromo and iodo ethyl ether.

The Action of Ethylene Oxide on the **Thioureas.**—Since ethylene oxide unites with primary and secondary amines to form a substituted amino-ethanol, it seemed possible that the thiourea might add the oxide either on the NH or the enol SH position. The experimental evidence indicates that the SH group alone is affected, yielding more or less stable thio ethers, $—N—C(=NR)S—CH_2CH_2OH$, or their hydrolysis products.

Ethylene oxide (35 g.) was added to a solution of the thiourea (38 g.) in acetone (200 cc.). The mixture was allowed to stand at room temperature for three weeks. On concentrating to half its volume and cooling, a yield of 25 g. of pure oxygen urea was obtained. The solution showed the presence of thioethylene glycol due to hydrolysis of the unstable thio ether. If the acetone solution of the oxide and thiourea was heated at 30–35° for forty-eight hours, there was found not only the oxygen urea but also an indefinite mixture of nitrogen and sulfur-containing products. With propylene oxide in acetone solution at room temperature the oxygen urea was formed. When heated at 60° there were isolated the urea and an oil (b. p. 128–135° at 11 mm.) whose sulfur content (21.7%) suggested that it might be an addition product of propylene-oxide and thiopropylene glycol, $HSCH(CH_3)CH_2OCH(CH_3)CH_2OH$. Phenyl oxygen urea (77% yield) and sulfur-containing oils were formed from ethylene oxide and phenylthiourea in acetone solution.

γ-Hydroxyethyl-diphenylthiourea.—A mixture of diphenylthiourea (100 g.), acetone (750 cc.) and ethylene oxide (50 g.) was heated at 50–55° for eighteen hours. On cooling, the ether crystallized out in transparent cubes which melted at 145°. The same compound had been isolated in small amount in the reaction product from ethylene iodohydrin and diphenylthiourea at 125°.

Anal. Calcd. for $C_{15}H_{16}N_2OS$: N, 10.30. Found: N, 10.32.

When heated the fused compound solidified at 148" and melted again at 220°; this latter compound proved to be impure diphenylurea.

That the compound (m. p. 145°) was a thio ether and not the isomeric **α,β-diphenyl-α-ethanol-thiourea**[12] was proved by its melting point, 145°, by the fact that hydrolysis

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[11] Dains, Brewster, Blair and Thompson, THIS JOURNAL, **44**, 2639 (1922).

[12] Dains, Brewster and others, *ibid.*, 47, 1983 (1925).

with alkali gave diphenylurea and that heating with halogen acids yielded again the diphenylurea and not diphenylthiazolidine.

Warmed in benzene solution, phenyl isocyanate united with the hydroxyl group, yielding a phenyl urethan (m. p. 101°).

Anal. Calcd. for $C_{22}H_{21}N_3O_2S$: N, 10.75. Found: N, 10.96.

On hydrolysis with alcoholic potassium hydroxide, only diphenylurea was obtained and not a triphenylbiuret which might have formed had the isocyanate reacted with an NH group.

Thiohydrolysis by Means of Potassium or Sodium Hydrosulfide.[13]—One of the characteristic properties of the isothiourea ethers is the ease with which they are hydrolyzed with alkalies, yielding oxygen ureas. An interesting analogous reaction has been developed in this investigation, *viz.*, thiohydrolysis, whereby thioureas can be obtained from these thio ethers.

Method for the Conversion of the β-Ethoxyethyl Ether of Thiocarbonyl Diphenyldiurea to the Diphenyl Amide of Thiourea-α,β-dicarboxylic Acid, $(C_6H_5NHCONH)_2$-CS—The thio ether (8 g.) was dissolved in hot alcohol (50 cc.) together with 5 g. of potassium hydrosulfide in water (10 cc.). Hydrogen sulfide was passed into the boiling solution for an hour. The hot solution was filtered and acidified with acetic acid. On cooling, fine needles of the thiourea (m. p. 202°) separated.

Anal. Calcd. for $C_{15}H_{14}N_4O_2S$: N, 17.85. Found: N, 17.85.

Using this method, thioureas in good yield were obtained from the following thio ethers: γ-methylphenylthiourea, γ-methyldiphenylthiourea and the 4-methyl ether of 1-phenyldithiobiuret.[14]

1,5-Diphenyl-dithiobiuret, which melts at 149°, was obtained from its methyl ether.[15]

Anal. Calcd. for $C_{14}H_{13}N_3S_2$: N, 14.64. Found: N, 14.63.

The Hydrolysis of Diacyl Thiourea Ethers.—When the γ-methyl ethers of dibenzoyl- or diacetylthiourea were treated with potassium sulfhydrate, complete hydrolysis occurred.[16]

y-Methyl Ether of Thiocarbonyl-di-urethan, $CH_3SC(NCOOC_2H_5)NHCOOC_2H_5$.—Methyl isothiourea sulfate (35 g.) was dissolved in water at 0°. To it was added slowly ethyl chlorocarbonate (60 g.) and potassium hydroxide (50 g.) in water solution with constant stirring. The resulting oil was extracted with ether. Upon evaporating the ether and cooling, the ether melting at 50–51° was obtained.

Anal. Calcd. for $C_8H_{14}N_2O_4S$: N, 11.97. Found: N, 12.14.

Its constitution was proved by conversion by means of liquid ammonia into symmetrical dicarbethoxyguanidine (m. p. 165°).

Thiocarbonyl-diurethan, $CS(NHCOOC_2H_5)_2$.—The greater stability of the carbethoxy over other acyl groups was indicated by the ready thiohydrolysis of the methyl ether (m. p. 51°). The carbethoxy thiourea melts at 111–112° and is soluble in alkalies, hot water and organic solvents. Previous efforts to synthesize the compound from thiophosgene and urethan had failed.

Anal. Calcd. for $C_7H_{12}N_2O_4S$: N, 12.73. Found: N, 12.75.

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[13] Lakra and Dains, THIS JOURNAL, 51, 2224 (1929).

[14] Johnson, *Am. Chem. J.*, 30, 174 (1903); Gentz, *Ann.*, 154, 44 (1870); Fromm, *ibid.*, 275, 34 (1893); Wunderlich, *Ber.*, 19, 452 (1886); Hecht, *ibid.*, 25, 756 (1892).

[15] Johnson, *Am. Chem. J.*, 30, 174 (1903).

[16] The diacetyl-γ-methylthiourea from methyl-isothiourea sulfate and acetic anhydride melts at 107–108°. N, 16.10. Found: N, 15.97.

α-Phenyl-α-carbethoxy-γ-methyl Thiourea, $C_6H_5N(COOC_2H_5)C(SCH_3)NH$, is formed from the interaction of γ-methylphenylthiourea, ethyl chlorocarbonate and alkali. It melts at 128° and on thiohydrolysis breaks down into thiocyanic acid mercaptan and phenylurethan.

Anal. Calcd. for $C_{11}H_{14}N_2O_2S$: N, 11.76. Found: N, 11.57.

Summary

1. The chlorohydrins, their esters and ethers react with thiourea giving y-thio ethers, which are easily hydrolyzed, the hydroxy derivatives being especially unstable. The thio ethers yield with amines guanidines, with acyl chlorides diacyl derivatives and with phenyl isocyanate the phenyl amide derivatives of α,β-thioureadicarboxylic acids.

2. A method has been described for the thiohydrolysis of the thio ether ethers.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE PARACHORS OF TWO ISOMERIC CHLORODINITROBENZENES

BY D. V. SICKMAN AND ALAN W. C. MENZIES

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It has been found by Sugden and his collaborators[1] that the parachors of isomerides which differ in structure only by the position of groups or linkages in the molecule are identical within the limits of experimental error. On examining the published data for surface tension, it was noticed that the values for the two isomers (A) 1-chloro-3,4-dinitrobenzene and (B) 1-chloro-2,4-dinitrobenzene differed very widely, the value for the latter being more than three times that for the former at like temperature. The reported densities differ by only a few per cent. As a consequence, the parachors of these two isomers, as computed from the available experimental data, show a wide divergence, namely, 258.7 for (A) and 346.4 for (B). The parachor computed from the atomic and structural parachors given by Sugden[2] is 358.3, and is, of course, identical for both substances.

Now the chloro-dinitrobenzenes differ considerably in reactivity, and they are known to exist in a number of different crystalline forms, so that a difference of parachor was not *a priori* unthinkable. Furthermore, it seemed hardly possible that experimental error could account for the enormous discrepancy found in surface tension, It therefore seemed worth while to redetermine the surface tensions and densities of the substance (A).

The existing values of surface tension and density for the two isomers (A)

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[1] (a) Sugden and Wilkins, *J. Chem. Soc.*, 127, 2517 (1925); (b) Sugden, "The Parachor and Valency," 1930, p. 33.

[2] Ref. 1b, pp. 38, 114.

and (B) are due, respectively, to Müller[3] and to Jaeger;[4] and these are the values recorded, for example, in "International Critical Tables." On studying the work of Müller, who worked with both isomers although he reported density and surface tension only for (A), a curious confusion became apparent. Müller's literature references for the preparation of the two isomers are interchanged. The three melting points which he found for the substance (A) are those of the substance (B); but the density, 1.471, at 60° which he reports as that of (A) is closer (difference 1.60%) to that found by us, 1.495, than it is (difference 2.65%) to that found by Jaeger, 1.511, for (B). It is therefore uncertain upon which isomer Müller's measurements of density and surface tension were carried out. In either case, however, the resulting experimental values for the parachor would be expected to be identical, which they are not.

The substance (A) was, accordingly, prepared[5] following the directions of Laubenheimer[6] and had a corrected melting point, for the a-form, of 36.3°, which is precisely that reported by Laubenheimer. We employed the capillary rise method for measuring surface tension in air, using a U-form apparatus of which one limb was of capillary core. Our experimental arrangements were such that, assuming the values given in "International Critical Tables" (1928) for benzene at 40, 50 and 60° as correct, we were able to confirm those given there for water at these temperatures within 0.3%. On account of its higher viscosity, the experimental values tabulated below for the substance (A) may be in error by perhaps 1%. Density was measured by a dilatometric method, with an estimated error within 0.1%. We tabulate our results below, along with those of Müller, adding the resulting values for the parachor.

TABLE I

SURFACE TENSIONS, DENSITIES AND PARACHORS OF 1-CHLORO-3,4-DINITROBENZENE

Temp., °C.	Surface tension dynes/cm.	Specific volume	Parachor Obs.	Parachor Calcd.	Observer
40	13.281	0.6712	259.5	358.3	Müller
50	12.782	.6757	258.7	358.3	Müller
60	12.301	.6803	258.0	358.3	Müller
		Av.	258.7	358.3	Müller
		Density			
40	45.1	1.516	346.0	358.3	S. and M.
50	44.6	1.505	347.8	358.3	S. and M.
60	44.2	1.495	349.3	358.3	S. and M.
		Av.	347.4	358 3	S. and M.

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[3] Müller, *Z. physik. Chem.*, 86, 224 (1914).

[4] Jaeger, *Z. anorg. allgem. Chem.*, 101, 117 (1917).

[5] We are indebted to Mr. A. E. Rainsford for his services in this connection.

[6] Laubenheimer, Ber., 8, 1623 (1875); 9, 760, 1826 (1876).

Our average value for this parachor is, therefore, 347.4 at a temperature of 50°. We are obliged to conclude that Müller's surface tension measurements are seriously in error, or that his specimen was impure.

For the substance (B), Jaeger[4] obtained in his lower temperature range the values noted below, using for surface tension the method of maximum bubble pressure. We have inserted the values for the resulting parachors.

TABLE II

SURFACE TENSIONS, DENSITIES AND PARACHORS OF 1-CHLORO-2,4-DINITROBENZENE

Temp., °C.	Surface tension dynes/cm.	Density	Parachor Obs.	Parachor Calcd.	Observer
60.4	45.5	1.515	347.1	358.3	Jaeger
76.2	43.9	1 497	348.1	358.3	Jaeger
95	42 2	1.477	349.4	358.3	Jaeger
			Av. 348.2		

The average value, 348.2, is for a temperature near 77°. Corrected for the drift of parachor with temperature, this would become 346.4 at 50°, a value not very different from 347.4, which is our experimental value for the other isomer.

Neither one of these values is especially close to the "calculated" value yielded by Sugden's adopted constants. The latter have been recalculated by Mumford and Phillips.[7] By using these newer constants, the discrepancy is not diminished, and the whole matter will be dealt with elsewhere.

From our comparison we conclude that the parachors at 50° of these two isomers are identical within the experimental error, while both fall short of the parachor calculated as the sum of the atomic and structural parachor terms of Sugden by 3.2%.

Summary.

1. The experimental data found in the literature yield for two isomeric chloro-dinitrobenzenes values of the parachor which are very widely divergent, while these would be expected to be identical.

2. By redetermination of densities and surface tensions, this discrepancy is shown to be due to experimental error.

3. The values of the two corrected parachors are shown to be very concordant, but to differ from the value calculated according to Sugden in a degree requiring explanation.

PRINCETON, NEW JERSEY

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[7] Mumford and Phillips, J. *Chem. Soc.*, 2112 (1929).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF PHENYLMAGNESIUM CHLORIDE IN THE ABSENCE OF A SOLVENT

BY HENRY GILMAN AND R. E. BROWN

RECEIVED MAY 5, 1930 PUBLISHED AUGUST 5, 1930

Introduction

Phenylmagnesium chloride has been prepared in satisfactory yield by customary procedures in ether as a solvent.[1] However, because of the relative inertness of the chlorine in chlorobenzene, the time (but not the attention) required for an approximately complete reaction is inordinate.

Details are given at this time for the preparation of phenylmagnesium chloride in 85% yields. The reaction is effected by heating chlorobenzene with magnesium in a sealed tube at 150–160° for three hours. The solid, "individual" phenylmagnesium chloride obtained in this manner is soluble in ether or in an ether–benzene mixture, and in such solutions can be employed to carry out the usual reactions of Grignard reagents.

Experimental Part

The technique followed in this preparation is essentially that of Gilman and Brown[2] for the preparation of magnesium diphenyl.

Eleven and two-tenths grams (0.1 mole) of chlorobenzene and 3.6 g. (0.15 atom) of magnesium[3] are placed in a bomb tube which can be prepared from a conventional Carius tube. The tube is evacuated by means of a good water pump until the chlorobenzene boils and then is sealed off. After heating at 150–160° for three hours, the liquid disappears entirely[4] and the tube is about one-half filled with a light brown powder.

Using the technique and operations described for the related preparation of magnesium diphenyl,[2] the contents of the tube were first washed with dry benzene, and then the phenylmagnesium chloride was dissolved in about 100 cc. of a mixture of equal parts of benzene and ether. The solution was filtered in an atmosphere of nitrogen[2] to remove unaltered magnesium, and aliquots were taken for titration.[5] The yield determined in this manner was 85%.

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[1] Gilman and St. John, Rec. trav. chim., 49, June (1930). Very probably the time required for this preparation might be significantly reduced with the use of higher-boiling solvents.

[2] Gilman and Brown, *ibid.*, 49, 202 (1930).

[3] The magnesium used in these experiments was of 30–80-mesh. However, it is highly probable that ordinary magnesium turnings will serve equally well. An excess of magnesium is unnecessary, but an excess of chlorobenzene may decompose the RMgX compound at elevated temperatures. This is strikingly illustrated in related experiments on the reaction between alkyl iodides and magnesium in the absence of a solvent.

[4] Heating at a higher temperature appears to be unsatisfactory because of a charring effect. Under our conditions, there appeared to be no reaction when the tube was heated at 140° for four hours.

[5] Gilman, Zoellner and Dickey, THIS JOURNAL, 51, 1576 (1929). Earlier references to this method for the quantitative estimation of organometallic compounds are to be found in this article.

Discussion of Method

The special procedure used here for a quantitative study is, of course, quite unnecessary in the usual manipulation of such ether-free Grignard reagents. This method of preparation has a number of advantages over the customary procedure. First, it makes it possible to prepare Grignard reagents from the relatively less expensive RCl compounds.[6] Second, the quantity of ether required in subsequent operations can be drastically reduced,' or possibly replaced by other less expensive and less inflammable solvents. These two advantages, in particular, are largely of technical importance. For ordinary laboratory operations the best procedure is that involving the use of bromobenzene in ether. Third, the method should lend itself to the synthesis of RMgX compounds having" alkyl or aryl groups, otherwise prepared with uncommon difficulty.[8]

The phenylmagnesium chloride prepared in this way is insoluble in benzene, but is soluble in ether or in an ether–benzene mixture. This significant observation should serve to correct numerous early observations on the chemistry of organomagnesium halides. Running through the literature of these compounds is the observation that once the ether has been expelled from the Grignard reagent (in high temperature reactions wherein a large part of the ether is replaced by a higher boiling solvent) it is difficult or impossible to again bring the RMgX compound into solution by means of ether. The insolubility referred to by such writers may be due to secondary reactions between the ether and RMgX and MgX_2 compounds, respectively. This remains to be determined.

We have mentioned that the Grignard reagent prepared in this manner should be brought into some sort of solution or suspension prior to its subsequent reaction with various reagents. This is quite necessary with dry gases, because the solid phenylmagnesium chloride appears not to react with carbon dioxide and gives but a small quantity of phenol in its reaction with oxygen.

The authors are indebted to Dr. E. C. Britton for helpful suggestions.

Summary

Directions are given for the satisfactory preparation of phenylmagne-

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[6] By this method it should be possible to obtain improved yields of RMgX compounds from such halides as *p*-bromodimethylaniline. Also, the yield of di-Grignard reagent from *p*-dibromobenzene should be significantly increased see [Gilman, Beaber and Jones, *Rec.* trav. *chim.*, 48, 597 (1929)]. It is interesting to note that when fluorobenzene is heated with magnesium at about 300° for many hours, a small quantity of diphenyl is formed. This means unquestionably that phenylmagnesium fluoride was formed as an intermediate compound. It is almost certain that phenylmagnesium fluoride can be prepared in this manner by heating at a lower temperature for a longer time.

[7] Gilman and McCracken, *ibid.*, 46, 463 (1927).

[8] A case in point is vinyl chloride. See also Ref 6 of this paper, and Evans and Diepenhorst, THIS JOURNAL, 48, 715 (1926).

sium chloride in the absence of solvents. General applications and conclusions from this sealed-tube method of preparation have been discussed.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OPTICALLY ACTIVE SALTS OF 2-NITRO-OCTANE

BY R. L. SHRINER AND J. H. YOUNG

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In connection with the general theory of tautomerism the conversion of an optically active secondary nitro compound into salts of the aci-form which are also optically active is of considerable theoretical importance. Only one example is recorded in the literature at the present time, namely, Kuhn's studies on 2-nitrobutane.[1] Since this work represents the only experimental evidence against the classical formulas for the aci-form, it was thought that the preparation and further study of another secondary nitro compound would furnish confirmatory evidence and additional knowledge concerning the tautomerism of these types of compounds.

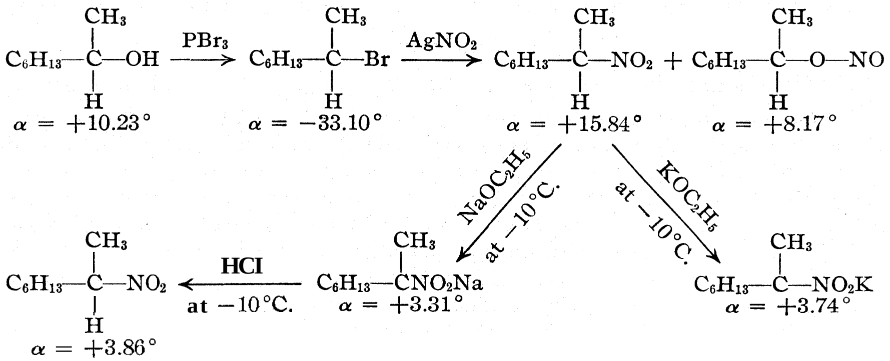
The following schematic diagram shows the preparation of the optically active 2-nitro-octanes and indicates the products obtained from them. It also lists the optical rotations of all the compounds and summarizes the results obtained during this investigation.

The dextro series represents the purer compounds. It is evident that a slight racemization took place during the preparation of the *l*-bromide from the *l*-octanol-2.

The above data fully confirm Kuhn and Albrecht's observation that the sodium salts of optically active secondary nitro compounds are also optically active. That this optical activity is actually due to the sodium salts was proved as follows.

(1) The optical rotation of equivalent amounts of the nitro compound

CHART I. DEXTRO SERIES



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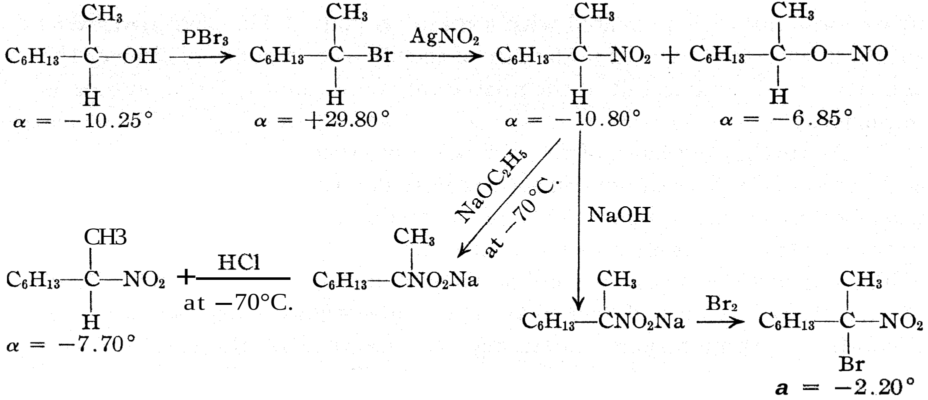
[1] Kuhn and Albrecht, *Ber.*, 60, 1297 (1927).

CHART II. LEVO SERIES.



and sodium ethylate reached a constant value as soon as the solutions were mixed. The reading remains constant over a period of twenty-four hours.

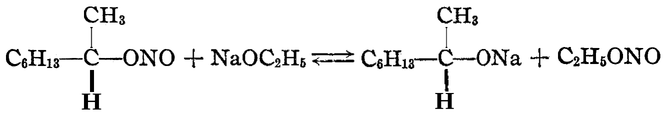
(2) The use of two equivalents of sodium ethylate gives exactly the same rotation as one equivalent. This shows that conversion to the salt is complete and that the observed activity is not due to unreacted nitro compound.

(3) The nitro compound can be regenerated from the sodium salt. The product so obtained has a lower rotation than the original nitro compound, 24% in case of the dextro, where the reconversion was carried out at −10°, and 71% in case of the levo, where the reconversion was carried out at −70°. The fact that the regenerated nitro compound was active at all shows that the sodium salt was active.

(4) The use of one and two equivalents of potassium ethylate gave optically active potassium salts whose rotations were the same (within experimental error) as those of the sodium salts. This shows that the metal used has no particular effect on the rotation of the aci-nitro form and hence the optical activity is due to the negative aci-ion.

(5) Treatment of the (1) sodium salt with bromine gave (1)-2-bromo-2-nitro-octane which was also optically active.

(6) The (d) octyl-2-nitrite which possessed a lower rotation than that of the nitro compound was also treated with sodium ethylate. The rotation observed as soon as possible was +3.46°, but on standing the rotation slowly increased to +6.00°. With two equivalents of sodium ethylate the rotation changed in the same manner except that a shorter time was necessary to reach the equilibrium value. This change in rotation was due to the saponification of the nitrite



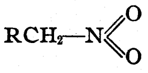
$$C_6H_{13}-\underset{H}{\overset{CH_3}{C}}-ONO + NaOC_2H_5 \rightleftharpoons C_6H_{13}-\underset{H}{\overset{CH_3}{C}}-ONa + C_2H_5ONO$$

This shows that the nitrite behaves in quite a different manner from the nitro compound when treated with sodium ethylate. No such increase in rotation was ever observed in the case of the nitro compounds and hence the activity of the sodium salt of the nitro form is not due to nitrite present as impurity.

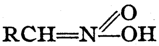
(7) As further evidence of the difference in structure between the nitro and the aci-form the absorption spectra were determined. The instrument used permitted measurement only in the visible range, but the absorption curves for the two forms were quite different.

The conversion of primary and secondary nitro compounds into salts of the aci-form has been discussed by many investigators and some of the theoretical considerations underlying the existence of these salts in an optically active state have been discussed by Kuhn and Albrecht.[1]

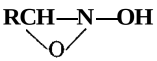
The following formulas (I), (II) and (III) are those given in most of the older work on these substances.



I



II



III

On the basis of the fundamental postulates of the electron theory, formulas (I) and (II) are impossible since they would place ten electrons in the valence shell of nitrogen. The classic formula (II) proposed by Nef[2] for the salts obviously cannot account for their optical activity. Structure (111), originally proposed by Holleman[3] and Hantzsch and Schultze,[4] has always been regarded as a possibility but never generally accepted chiefly because the existence of such carbazoxy rings has never been absolutely established.[5] Auwers and Harris[6] have attempted to use refractometric data as a means of determining the structure of nitro compounds and certain oxygen-alkyl derivatives which may possibly have the ring structure, but the results obtained are not conclusive. In any case, it is clear that (III) contains an asymmetric carbon atom which would account for the activity of the salts.

Since the classical formulas (I) and (II) are inconsistent with the postulates of the octet theory it is necessary to consider electronic formulas in order to obtain an explanation of the above experimental data

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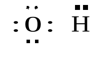
[2] Nef, Ann., 280,263 (1894).

[3] Holleman, *Rec. trav. chim.*, 13,405 (1894); 14, 129 (1895).

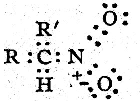
[4] Hantzsch and Schultze, *Ber.*, 29, 699, 2251 (1896).

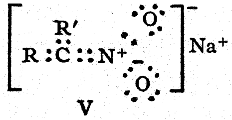
[5] Perhaps the best examples of such carbazoxy rings are the nitrogen ethers of the oximes. Beckmann, Ann., 365, 201 (1909); Scheibler, *ibid.*, 365, 215 (1909). Even these may be written in a non-cyclic form by means of the electron theory

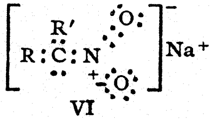


$$\mathrm{R}:\underset{:\ddot{O}:}{\underset{\cdot\cdot}{N}}::\underset{H}{\underset{\cdot\cdot}{C}}:\mathrm{R}.$$

[6] Auwers and Harris, *Ber.*, 62,2281 (1929); 57,454,459 (1924).


IV


V


VI

Structure (IV) is the one favored by Sugden as the result of the parachor for nitro compounds.[7] Structures (V) and (VI) represent two possibilities for the salts, (V) being regarded by Sugden as the most probable and (VI) being used by Kuhn[1] to explain his results.

It will be noted that (V) contains no asymmetric atoms and hence is not capable of existing in optically active forms whereas in (VI) the carbon atom is asymmetric and hence optical activity is possible. It is therefore very probable that the activity of the salts is due to the presence of the asymmetric ion[8] (VI).

Although the presence of this asymmetric ion explains very well the optical activity observed, there remains to be considered the fact that a very marked drop in optical rotation occurred when the nitro compound was converted to the salt. Also the nitro compound regenerated from this salt possessed a lower rotation than the original and hence was a mixture of the racemic modification with some of the active form. These facts raise the question as to the possibility of the presence of the other ion (V) in the solution also. While the data in the present investigation are not conclusive on this point, its presence must be considered as a possibility. Form V is not optically active, hence if both (V) and (VI) were formed on addition of sodium ethylate then any activity would be due to (VI) alone. The low rotation of the salts is then easily explained since only a small percentage of the salt would exist in this form (VI). This is supported by the fact that in regenerating the nitro compound from the salts, Form (V) would give the racemic modification of (IV) while (VI) would give the active form. It will also be noted that the rotation of the nitro compound regenerated at −10° was only 24% of the original whereas at −70° the rotation was 71% of that of the original nitro compound. This would indicate that at the lower temperature a higher percentage of (VI) was present. Form (VI) would also explain the ready formation of the optically active bromo-nitro compound by the action of bromine on the sodium salt.

The other explanation for the low rotations of the salts and regenerated nitro compounds is that racemization took place during the formation of the salt and regeneration of the nitro compound. This might seem to be the explanation for the temperature effect mentioned above. However, the

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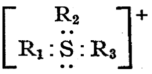
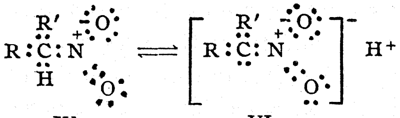
[7] Sugden, J. *Chem. Soc.*, 122,1525 (1925).

[8] The authors are indebted to one of the reviewers for pointing out that this asymmetric ion (VI) is analogous to the optically active sulfonium ions of the type shown.

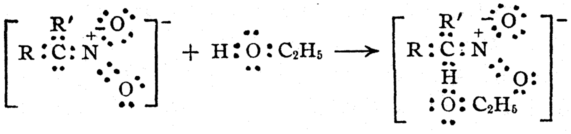


fact that the rotations of the salts were remarkably constant over a period of *twenty-four hours* would seem to discount the racemization theory and favor the idea that there exist two forms of the aci-nitro ion, (V) and (VI). This is in agreement with the work of Branch and Deelman,[9] who studied the change in conductivity which took place on the addition of hydrochloric acid to the sodium salt of the aci-nitro compound. An abnormal conductance drop took place at the start followed by a slow gradual drop for the conversion of the greater part of the aci-nitro salt back to the normal nitro form. Branch and Deelman suggest Form (III) for that portion which caused the rapid initial drop. Whether Form (III) or (VI) is correct cannot be stated at the present time, but the experimental data on both conductivity and optical activity can be correlated by postulating the presence of two different forms of the negative ion. The chief objection to such an assumption is the fact that racemization of VI does not occur readily, which means that the ions V and VI are not in rapid equilibrium with each other. While at first this may seem unlikely, it is not impossible if the following mechanism for ion formation is considered. (1) Partial ionization of the nitro form to give the asymmetric ion VI

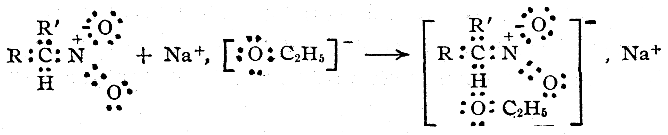


IV VI

This ion is probably stabilized by solvation



or, the same solvated ion may be produced by the direct combination of the nitro compound with the ethylate ion:



The temperature effect discussed above is good evidence in favor of stabilization of this asymmetric ion by combination with the solvent since solvation is known to be dependent on the temperature. This combination of VI with a molecule of alcohol prevents its conversion to the inactive ion V. *(2)* Primary rearrangement followed by ionization to give the inactive ion V.

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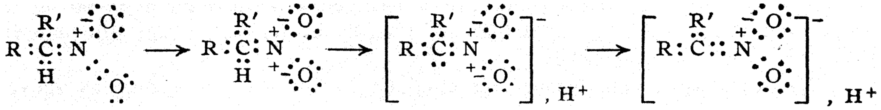
[9] Branch and Deelman, THIS JOURNAL, 49, 1765 (1927).



IV VII V

This rearrangement of IV to VII parallels the conversion of a ketone into its active form, *i. e.*, changing the non-polar oxygen into a semi-polar oxygen atom.[10]

From an electronic point of view, Form (V) should be formed in preference to Form (VI), since it represents a more stable arrangement and electron distribution. This agrees with the experimental facts that only a small part of the salt is active and only a portion of the regenerated nitro compound is active.

Experimental

Preparation of d- and *l*-Octanol-2.—Octanol-2 was resolved by crystallization of the brucine salts of the phthalic acid ester according to the procedure given in "Organic Syntheses."[11] The d-octanol-2 distilled at 86° at 20 mm.; α_D^{25} +10.23°; and l-octanol-2 at 84° at 16 mm.; α_D^{25} −10.25°.

***l*-2-Bromo-octane.**—In a 500-cc. three-necked flask fitted with a stirrer, a thermometer reaching to the bottom of the flask and a separatory funnel, was placed 39 g. of d-octanol-2. The alcohol was cooled to −5° by means of an ice-salt bath and 90 g. of phosphorus tribromide was added drop by drop so that the temperature did not rise above +5°. The mixture was allowed to stand overnight and slowly come to room temperature. It was then heated on a boiling water-bath for one hour and cooled. The mixture was decomposed with 200 cc. of ice water and the bromide taken up in ether. The ether solution was dried and the ether distilled. The residual oil was vacuum distilled; 47 g. of *l*-2-bromo-octane boiling at 83–84° at 18 mm. was obtained; α_D^{25} −33.1°; n_D^{20} 1.4500; yield, 80%.

d-2-Bromo-octane.—This isomer was obtained by exactly the same procedure; 49 g. of *l*-octanol-2 yielded 62 g. of d-2-bromo-octane; b. p. 83–84' at 18 mm.; α_D^{25} +29.8; n_D^{20}, 1.4501; yield, 85.3%.

d-2-Nitro-octane.—Eighty cc. of dry benzene and 60 g. of finely powdered silver nitrite were placed in a 200-cc. three-necked flask fitted with a stirrer, reflux condenser and dropping funnel. The mixture was cooled to 0° and 47 g. of *l*-2-bromo-octane run in slowly with stirring. The reaction mixture was stirred for three hours at 0° and then heated on a water-bath for six hours. The benzene solution was decanted and the residue washed with two 25-cc. portions of benzene. The benzene was distilled and the mixture of 2-octyl nitrite and 2-nitro-octane was carefully fractionated in *vacuo* by the use of a modified Claisen fractionating flask. After three fractionations 5.5 g. of d-2-nitro-octane was obtained as a light yellow oil; b. p. 102–105 at 23 mm.; yield, 14.4%; d_{20}^{20} 0.9224; n_D^{20}, 1.4324; M_D (calcd.), 45.65; M_D (found), 44.75; α_D^{25} +15.84 (abs. ethyl alcohol).

Anal. Subs., 0.1042: CO_2, 0.2308; H_2O, 0.0996. Calcd. for $C_8H_{17}NO_2$: C, 60.37; H, 10.69. Found: C, 60.41; H, 10.62.

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[10] Carothers, THIS JOURNAL, 46, 2229 (1924); Shriner, Struck and Jorison, ibid., 52, 2064 (1930).

[11] "Organic Syntheses," J. Wiley and Sons, Inc., New York, 1926, Vol. VI, p. 68.

The d-2-octyl nitrite obtained was also a light yellow oil distilling at 86–90° at 18 mm.; yield, 9.8 g. or 25.6%; d^{20}_{20} 0.852; n^{20}_{D} 1.4279; M_D (calcd.), 45.25; M_D (found), 47.7; α^{25}_{D} +8.17° (abs. alcohol).

1-2-Nitro-octane.—The isomer was obtained by the same procedure as above; 60 g. of d-2-bromo-octane and 60 g. of silver nitrite yielded 7.4 g. of 1-2-nitro-octane; yield, 15.0%; b. p. 100–103° at 18 mm.; d^{20}_{20} 0.9165; n^{20}_{D} 1.4292; M_D (calcd.), 45.65; M_U (found) 44.65; α^{25}_{D} −10.8" (abs. alcohol).

The *l*-2-octyl nitrite was obtained in 24.1% yield; b. p. 85–90' at 18 mm.; d^{20}_{20} 0.857; n^{20}_{D} 1.4218; M_D (calcd.), 45.25; M_D (found), 46.8; α^{25}_{D} —6.85" (abs. alcohol).

Sodium Salt of d-2-Nitro-octane.—A standard solution of sodium ethylate in absolute ethyl alcohol was prepared by dissolving metallic sodium in absolute alcohol. A sample of 0.2840 g. of d-2-nitro-octane was mixed with 4.44 cc. of 0.416 *N* sodium ethylate solution (1 equivalent) and then diluted to 20 cc. The rotation was observed immediately and at one-hour intervals over a period of twenty-four hours, during which time the readings were constant within the experimental error of reading. All rotations were made with D sodium light and at 25°; average, α^{25}_{D} +3.31°.

A second solution was prepared using 0.3016 g. of d-2-nitro-octane and 9.10 cc. of 0.416 N (2 equivalents) sodium ethylate solution. The readings were again constant over a period of twelve hours; average, α^{25}_{D} +3.29°.

Potassium Salt of **d-2-Nitro-octane.—Equivalent** quantities of a standard solution of potassium ethylate in absolute alcohol and d-2-nitro-octane were mixed and the rotation was observed over *a* period of twenty-four hours. The readings were constant; average. α^{25}_{D} +3.74°.

With two equivalents of potassium ethylate the optical activity of the solution also remained constant over a period of 23 hours; average, α^{25}_{D} +3.96°.

Preparation of *l*-2-Bromo-2-nitro-octane.—(a) To 1.0 g. of I-2-nitro octane was added 25 cc. of 0.3286 N sodium ethylate. Aqueous bromine was added until the solution became permanently yellow. The reaction flask was cooled in a freezing mixture. The solution was allowed to stand for five minutes, after which enough sodium thiosulfate was added to remove the color of the bromine; 25 cc. of water was added and then 100 cc. of ether to extract the product. The ether solution was dried and the ether evaporated at room temperature by use of suction. The air stream was purified by use of an askarite–dehydrite tube; 0.3087 g. of the residue of *l*-2-bromo-2-nitro-octane was tested for rotation; α^{25}_{D} −2.92°.

(b) A second sample of 2 g. of 1-2-nitro-octane was treated with an excess of dilute aqueous sodium hydroxide. The aqueous solution was washed once with ether to take out any unreacted 1-2-nitro-octane. The aqueous layer was separated and treated with an excess of bromine. The *l*-2-bromo-2-nitro-octane obtained had a very irritating odor; α^{25}_{D} −2.22°; n^{20}_{D} 1.4499; d^{20}_{20} 1.113; M_D (calcd.), 54.5; M_D (found), 57.4.

Anal. Subs., 0.3376: 15.37 cc. of 0.0935 N $AgNO_3$. Calcd. for $C_8H_{16}BrNO_2$: Br, 33.60. Found: Br, 34.05.

Reaction of d-2-Octyl Nitrite with Sodium Ethylate.—A sample of 0.3103 g. of d-2-octyl nitrite was treated with an equal molal quantity of sodium ethylate (2.63 cc. of 0.740 N). Readings were made over a period of one hundred hours. The readings changed from an initial value of α^{25}_{D} +3.46° to a maximum of α^{25}_{D} +6.00°. Longer standing caused the rotation to drop slightly. A sample of 0.3215 g. of d-2-octyl nitrite was treated with two equivalents of 0.740 N sodium ethylate. The average of ten readings over an eighty-hour period gave α^{25}_{D} +6.15°. The initial reading was α^{25}_{D} +5.71°.

Conversion of the Sodium Salt of d-2-Nitro-octane Back to d-2-Nitro-octane by an Addition of Acid at −10".—(a) A 0.4575-g. sample of d-2-nitro-octane was made up to 20 cc. volume by adding 95% alcohol. The rotation was taken and found to be α^{25}_{D}

+12.35° instead of +15.84° (abs. alcohol). The solution was then treated with 2.33 cc. of 1.233 *N* sodium ethylate at −10°. An excess of alcoholic hydrogen chloride (6.5 cc. of 0.616 *N*) was then added and just enough water (2 cc.) to dissolve the sodium chloride formed in the reaction. The solution was diluted to 40 cc. with 95% alcohol and 20 cc. (0.2289 g. of d-2-nitro-octane) used for taking a rotation. Readings were made over a period of eighteen hours; average, α_D^{25} +3.86°. This is 24.12% of the rotation of the unreacted d-2-nitro-octane.

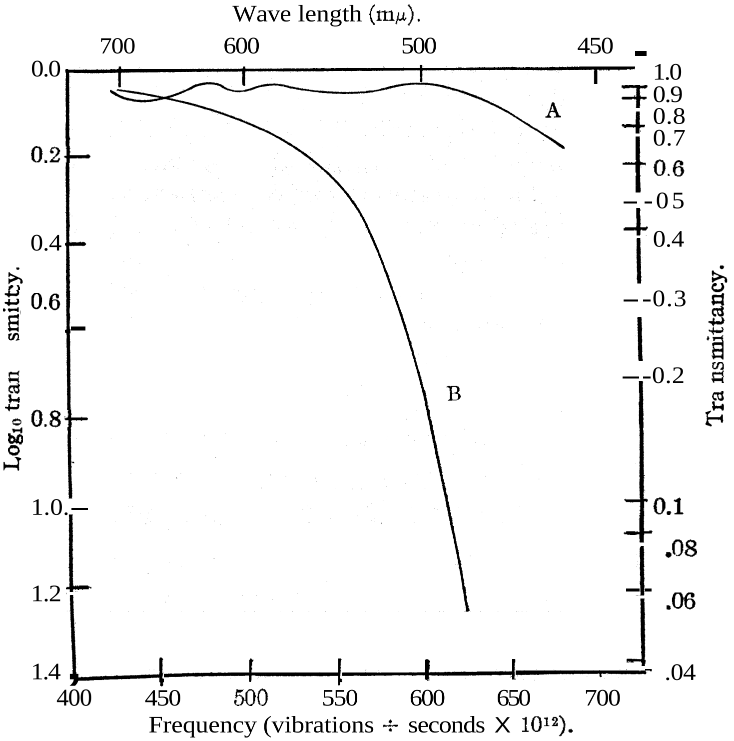

Plate I.—Absorption spectra of d-2-nitro-octane and its sodium salt.

(b) To remove the effect of the water on the rotation, the other 20-cc. portion after the addition of the acid was diluted with water and the d-2-nitro-octane extracted with 25 cc. of ether. The ether solution was dried with anhydrous magnesium sulfate. The ether was distilled off and the residue dissolved in absolute alcohol. This gave α_D^{25} +2.86°. Part of the nitro compound was probably lost due to slight solubility in the alcohol–water layer.

Conversion of the Sodium Salt of 1–2–Nitro-octane **Back** to I–2–Nitro-octane at Temperature of Carbon Dioxide Snow (−70°).—To 0.5 g. of I-2-nitro-octane was added an excess (10 cc. of 0.3286 *N*) of sodium ethylate. The solution was cooled by carbon dioxide snow and an excess of alcoholic hydrogen chloride added. The reaction mixture was allowed to stand for ten minutes in carbon dioxide snow. Water was added and the I-2-nitro-octane extracted with ether. A 0.3462-g. sample of the recovered 2-nitro-octane was made up to 20 cc. volume with absolute alcohol and the rotation taken: α_D^{25} −7.7°, or 71.2% of the unreacted 1-2-nitro-octane.

Absorption Spectra of d-2-Nitro-octane **and** the Sodium Salt of d-2-Nitro-octane.—The absorption spectra (Plate I) were determined in a K and E color analyzer which permitted measurements in the visible range only. A solution of 0.5191 g. of d-2-nitro-octane in 20 cc. of absolute alcohol was used for obtaining **curve (A)** and a sample of 0.5041 g. of 2-nitro-octane which was treated with one equivalent of sodium ethylate solution and diluted to 20 cc. was used to obtain curve (B).

Summary

1. The preparation of (*d*) and (I) 2-nitro-octanes is described.
2. The sodium and potassium salts of d-2-nitro-octane were found to be optically active to the same extent.
3. The d-2-nitro-octane regenerated from the sodium salt at −10° was optically active to the extent of 24.12% of the original d-2-nitro-octane.
4. By use of very low temperature for the reaction, the regenerated *l*-2-nitro-octane was optically active to the extent of 71.2% of the original I-2-nitro-octane.
5. Optically active d-2-bromo-2-nitro-octane was prepared from the active sodium salt of d-2-nitro-octane.

URBANA, ILLINOIS

[CONTRIBUTION PROM THE ZOOLOGY DEPARTMENT, UNIVERSITY OF WISCONSIN]

THE RELAXATIVE HORMONE OF THE CORPUS LUTEUM. ITS PURIFICATION AND CONCENTRATION[1]

BY H. L. FEVOLD, FREDERICK L. HISAW AND R. K. MEYER

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It is a matter of common knowledge, at least among those versed in the physiology of reproduction, that the pelvis of several species of mammals is modified during pregnancy to facilitate the birth of young. These pelvic modifications commonly involve the ligaments of the symphysis pubis and ilio-sacral unions in a fashion which enables these bones to move apart and thus increase the diameter of the pelvic canal. In some animals, only the ilio-sacral unions are changed, while in others both these and the symphysis pubis are affected. One of the most striking examples of this phenomenon is found in pregnant guinea pigs. The pelvic ligaments of these animals begin to show signs of loosening, both at the ilio-sacral and pubic regions, about the middle of pregnancy and they become more and more pronounced with the approach of parturition. At the termination of pregnancy the ilia can be freely moved, and a finger can be placed between the pubic bones at the symphysis. This remarkable modification of the guinea pig pelvis has, for lack of a better term, been designated as ligamentus relaxation.

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[1] This work has been assisted by grants from the committee for Research on Problems of Sex of the National Research Council.

It was not until quite recently that these pregnancy changes were found to be under hormonal control.[2] It was first discovered that a substance was present in the blood of pregnant rabbits which, when injected into virgin guinea pigs during oestrum, would produce ligamentus relaxation, characteristic of that which normally occurs during pregnancy. This substance appears in the blood of pregnant rabbits, at about the seventh day of the gestation period, in sufficient amount to give a positive test when 2 cc. of serum is injected and disappears within twelve hours after the birth of young. So constant is the presence of this relaxative substance and so definite is its reaction that it may be used as a test for pregnancy in rabbits.

Although the chemical and physiological properties of the relaxative substance were first studied as it exists in the blood, it was later demonstrated that the substance had its origin in the corpora lutea and placenta. It is a hormone typical of the corpus luteum but, like the follicular hormone "oestrin," may also have other sources, particularly the placenta. The hormone is not species specific, but is found in the blood and tissues of certain mammals in greater amounts than in others.[2] However, no matter where it is found it can be extracted and purified by essentially the same chemical procedures.

The only physiological property thus far discovered for this hormone is its action on the pelvic ligaments and for this reason we propose the name "Relaxin." This designates its physiological activity and also adheres to the generally accepted nomenclature for hormones.

The factors governing the relaxation reaction can best be demonstrated in castrate virgin guinea pigs. When such animals are injected with relaxin the pelvic ligaments do not respond, but if they are first brought into artificial oestrum through the use of follicular hormone and are then given relaxin, positive results follow. The follicular hormone must first produce its effect before relaxin can act. If relaxin is given first, followed by follicular hormone, no relaxation occurs and when both hormones are given simultaneously over an extended period, the results remain negative until enough time has elapsed for the follicular hormone to put the animal in the proper physiological condition, so that the pelvic ligaments will respond to relaxin. Relaxation of the pelvic ligaments of the guinea pig depends upon the action of two hormones, namely, oestrin and relaxin, neither of which can produce the reaction when given alone, but the two must work in definite relationship to each other.

It also seems that oestrin and relaxin work with each other in a qualitative fashion in achieving and prolonging the ligamentus relaxation reaction. This idea is supported by the fact that a castrate female need not be brought into full oestrum before the relaxative hormone can function,

[2] **Frederick** L. Hisaw, *Phys. Zoology,* **2,** 59 (1929).

nor can the action of this hormone be hindered by large doses of oestrin. It is also true that once the relaxed condition is attained, relaxin alone cannot maintain it over an extended period, but can do so only when the animal is kept tuned up, so to speak, by frequent doses of oestrin.

The potency of different preparations of relaxin is standardized in terms of their ability to produce relaxation of the pelvic ligaments of virgin female guinea pigs which are in full oestrum. These animals are injected subcutaneously with a definite amount of the preparation to be tested and after ten to twelve hours the pelvic ligaments are palpated gently to see if they have become loose. Loosening can best be determined by alternately moving each half of the pelvis up and down vertically while at the same time keeping a finger over the symphysis pubis. The minimum amount of hormone which causes a definite loosening of the ligaments within ten to tweve hours after a single injection is taken as a guinea pig unit.

This paper deals only with the relaxative hormone of the corpus luteum, but it should be mentioned in passing that relaxin is only one of two hormones elaborated by the corpora lutea of the sow. This second hormone differs from relaxin in both its physiological and chemical properties. It does not produce relaxation but is responsible for various other reactions such as the growth of placentomata,[3] inhibition of ovulation and vaginal changes typical of pregnancy,[4] progestational development in the uterus of rabbits,[5,6] and formation of a premenstrual endometrium in the uterus of castrate monkeys.[7] This second hormone also depends upon the cooperation of oestrin to produce its effect in a manner similar to that described for relaxin, with the exception that the relationship here is a quantitative one.[8] The two corpus luteum hormones have been separated from each other quantitatively and the chemical nature of the second hormone is being studied at the present time. We wish only to state that it has been obtained in a highly purified, water-soluble condition.[9]

General Characteristics of Relaxin.—The relaxative hormone is extracted from corpora lutea, which is its chief source, or from other tissues, by means of acid alcohol. The extract is subsequently purified by elimination of proteins, phospholipins and other fatty substances by various methods with the result that *a* water-soluble extract, containing the active principle in concentrated form, is obtained. The hormone may then be obtained from this extract by either of two different methods. By crystallization of the evaporated aqueous extract from glacial acetic acid, the

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[3] C. K. Weichert, *Proc. Soc. Exptl. Biol. Med.*, 25, 490 (1928).

[4] Frederick L. Hisaw, R. K. Meyer and C. K. Weichert, *ibid.*, 25, 754 (1928).

[5] G. W. Corner and W. M. Allen, *Am. J. Physiol.*, 88, 326 (1929).

[6] W. M. Allen and G. W. Corner, *Proc. Soc. Exptl. Biol. Med.*, 27, 403 (1930).

[7] Hisaw, Meyer and Fevold, *ibid.*, 27, 400 (1930).

[8] Hisaw and Leonard, *Am. J. Physiol.*, 92, 574 (1930).

[9] Fevold, Hisaw and Meyer, *Proc. Soc. Exptl. Biol. Med.*, 27, 606 (1930).

hormone is obtained in a form in which it is associated with sodium chloride. The product is crystalline in nature and consists largely of sodium chloride. The active material is present in this crystalline preparation but whether it is merely adsorbed on the crystals or crystallized with the sodium chloride is open to question. Approximately one milligram of this crystalline material is sufficient to give the physiological reaction described above. On the other hand, the hormone may be precipitated from solution by means of picric acid and subsequently purified, with the result that a product is obtained which is effective in about 0.03-mg. doses. One gram of the purified material contains about 28,000 guinea pig units.

The purified hormone is soluble in glacial acetic acid, only slightly soluble in distilled water and 95% alcohol, insoluble in 99% alcohol and other organic solvents such as ethyl ether, acetone, petroleum ether and benzol. In its impure form it is sufficiently soluble in 95 or 97% alcohol so that these solvents may be used to purify the crude extract. The hormone dissolves in aqueous alkaline or acid solutions. In alkaline solution, however, above a PH of 9.0, the activity of the hormone is impaired quite rapidly, while in 2% sodium hydroxide the hormone is destroyed almost immediately. In acid (non-oxidizing) and neutral solutions the hormone is stable. Solutions at PH of 7.0 and 3.2 have been kept in the ice box for a year with no detectable decrease in activity.

The hormone is also affected by oxidation, by drying in air and by heating. Solutions of the hormone decolorize potassium permanganate with consequent loss of activity. One cc. of a $N/10$ solution of potassium permanganate will inactivate completely 25 G. P. units of the hormone. Dilute nitric acid renders it inactive, as do also bromine, chlorine and iodine. If the hormone is permitted to stand at room temperatures in dry form the activity decreases slowly but definitely, If the dry hormone is heated under atmospheric conditions over 50° the activity is completely lost in twenty-four to forty-eight hours. Heating the aqueous solutions at 70–80" for five or six hours destroys all activity, while boiling for ten or fifteen minutes brings about the same result.

Some of the properties of the active material would point to a peptide-like structure while other characteristics seem to eliminate that possibility. It has both basic and acidic properties, since it is soluble in both acid and alkaline solutions. It has a very definite isoelectric point, being precipitated from a 0.1% solution at a PH of 5.4–5.5. Proteolytic enzymes break down the material to a stage where it is no longer active. Trypsin and pepsin both destroy the hormone. It contains nitrogen but the amount is rather low to correspond to a peptide-like structure. A 0.5% solution of the active material is negative to Millon's reaction and to the ninhydrin reaction, but gives a faint violet coloration with Poser's ring biuret test. It is also negative to Molisch's reaction.

Experimental Details

Extraction of Corpus Luteum Tissue.--The following describes the preparation of an extract of one kilogram of corpus luteum tissue from sows' ovaries.

Corpora lutea from sows' ovaries are finely ground and extracted twice, for forty-eight hours, with two liter portions of acidulated alcohol (2 cc. of concd. hydrochloric acid to 98 cc. of 95% alcohol) at room temperature, with frequent shaking and stirring. After each extraction the residue is pressed dry by means of a press. The two extracts are united and one-third of their volume of water is added. The fatty material which separates is filtered off and discarded.

The filtrate is adjusted to a P_H of 6.8 by the careful addition of 10% sodium hydroxide. When the end-point is being approached, the extract becomes turbid and at a P_H of 6.8 a flocculent precipitate separates out. After standing for a few hours (six to eight) the precipitate is filtered off, reextracted with 200 cc. of 70% alcohol, which has been acidified as before, reprecipitated by neutralization and discarded.

The united extracts are evaporated to a semi-dryness under reduced pressure at 40 to 45° or preferably in an air dryer at 40° and extracted with 450 cc. of 95% alcohol, using 150-cc. portions in three successive extractions, allowing one-half hour for each extraction. The insoluble residue is centrifuged off and discarded while the alcoholic solution is evaporated and the residue emulsified in 200 cc. of water. Phospholipins are precipitated by adding an equal volume of acetone, removed and discarded.

The aqueous acetone solution is again evaporated and the residue extracted with 200 cc. of 97% alcohol. The material must be triturated with the alcohol until it is in a finely divided condition. A large volume of alcohol must not be used as this results in a partial precipitation of the hormone. After removal of the alcohol as before, the solute is repeatedly extracted with ether or acetone to remove any remaining fats. The ether-insoluble residue is then dissolved in water at a P_H of 3 to 4. The water solution is clear and light brownish in color. It is usually prepared so that 1 cc. is equal to 15 g. of the fresh tissue, although it can be concentrated to more than twice that strength. As a rule, enough of this extract to represent one gram of the fresh tissue is sufficient to give a good positive result in the relaxation reaction. This extract has been used for a long time in our laboratory and has proved very satisfactory. We shall designate this preparation as preparation "A."

If the residue after the ether extraction is dissolved in a small amount of 95% alcohol and then diluted with 99% alcohol until no more precipitate forms, the relaxative hormone is completely precipitated. The precipitate is somewhat soluble in distilled water but much more readily soluble in water at a P_H of 3 to 4 (prepn. "B"). The potency of this preparation is the same as that of the original extract. Table I shows the number of units contained in preparation "A" from one kilogram of tissue and in preparation "B" after precipitation.

TABLE I

RELATIVE POTENCY OF PREPN. "A" AND PREPN. "B"

Sample. .	1	2	3	4	5
Prepn. "A," units per kilo.	1100	975	1000	800	850
Prepn. "B," units per kilo.	1100	950	1000	750	850

The Relaxative Hormone in the Blood of Pregnant Rabbits.—The presence of the relaxative hormone in the blood of various pregnant animals has been previously reported.[2] The amount increases with the duration of pregnancy, being greatest during the last half of the gestation period.

At this time 2 cc. of pregnant rabbit serum is sufficient to produce very pronounced relaxation, while 0.25 cc. ordinarily gives a positive reaction.

The hormone can be obtained from rabbit serum by various methods. If the serum is evaporated to semi-dryness, the active material can be extracted by means of saline solution. Ninety-five per cent. alcohol will not extract the hormone from the dried residue, but if the residue is treated with 95% alcohol which has been acidified as previously described, the hormone is taken into solution. After neutralization and evaporation, the residue is then soluble in neutral 95% alcohol.

To determine the type of material with which the hormone is associated in the blood, the following experiments were carried out. The globulins of the blood serum were precipitated, using sodium sulfate as the precipitant. The globulin-free serum was found to be inactive, while the globulin fraction produced relaxation. The euglobulins were then precipitated by the addition of 13 to 14% sodium sulfate. In this case the precipitated fraction was inactive while the remaining serum retained its activity. It appears, therefore, that the hormone was associated with the pseudoglobulin fraction of the serum proteins. To test this further, the entire globulin fraction was precipitated from a sample of pregnant rabbit serum by one-half saturation with sodium sulfate. They were then fractionated by fractional precipitation with the same precipitant. As before, the fraction designated as the euglobulins was inactive while the pseudoglobulins contained the hormone.

Preparation of the Hormone Associated with Sodium Chloride.—The ether-insoluble material from one kilogram of fresh tissue is dissolved in 200 cc. of glacial acetic acid. The solution is then permitted to evaporate slowly, in the air dryer, until all the acetic acid has been removed and crystals of a definite form appear. These crystals are insoluble in ethyl alcohol, so the brown sirupy material is removed by dissolving in 50 cc. of 99% alcohol. Here again the volume must be kept small. If a large volume of alcohol is used, a flocculent precipitate will appear. This precipitate dissolves if the volume of alcohol is small, while the crystals remain insoluble. To remove any traces of the flocculent precipitate, the following procedure is used. The 50 cc. of alcoholic extract is diluted with 99% alcohol until no more precipitate forms, the precipitate is centrifuged off, and the alcoholic solution again concentrated to 50 cc. The impure crystals are then reextracted, using the alcoholic solution as the solvent. Any of the flocculent material which remained will dissolve. After this has been repeated twice, the crystals are washed several times with absolute alcohol, leaving them in a "pure" condition. Microscopically nothing remains but the crystalline material. The crystalline fraction contains the relaxative hormone while the alcohol solution is relatively inactive. Approximately 85% of the hormone is obtained in the crystalline fraction while 15% remains in the alcoholic solution. This can be completely removed by the addition of a small amount of sodium chloride and recrystallization from acetic acid. The crystals in this case are, however, as a rule irregular and contain an excess of sodium chloride.

The crystalline product is composed of approximately four parts ash and one part volatile material. The ash is made up of sodium chloride, as is shown by the following facts. If the ash is dissolved in a little water and crystallized on a slide, characteristic crystals of sodium chloride appear. If the chlorine in the ash is determined and calculated as sodium chloride the results agree with the weight of the ash. Also, the crystals give a strong sodium test while tests for other cations of non-volatile chlorides have been negative. The volatile fraction contains the active material which, as we shall see later, contains a definite amount of nitrogen.

The crystals dissolve readily in water. When this aqueous solution is injected, in the same proportion as that given for the tissue extract, it produces relaxation of the pelvic ligaments of guinea pigs in oestrum. The dose which gives a positive reaction represents approximately one milligram of crystalline material or two-tenths of a milligram of volatile material. The amount of crystalline material obtained, in different preparations, from the same amount of tissue, is relatively constant although not entirely so. One kilogram of corpus luteum tissue yields approximately 0.8 g. of crystalline material, varying in individual preparations by ±0.2 g.

Purification of the Hormone by Precipitation with Picric Acid.—The aqueous solution of the crystalline material is made acid (*P*H 4 to 5) with hydrochloric acid and an excess of picric acid is added. A precipitate is formed which is separated by centrifuging. The precipitate is washed several times with distilled water, dissolved by adding just enough sodium hydroxide to cause solution and reprecipitated by making acid with hydrochloric acid. The product is insoluble in water, alcohol and ether but dissolves in glacial acetic acid. It retains the activity of the original preparation quantitatively, as is shown by Table II.

TABLE II

RELATIVE POTENCY OF CRYSTALLINE PREPARATION AND PICRIC ACID PRECIPITATE

Sample	1	2	3	4	5
Crystalline prepn., G. P. units	700	800	850	770	800
Picric acid prepn., G. P. units	700	800	835	740	775

While this insoluble picrate was first prepared from the crystalline preparations, it was later found that the hormone could be precipitated and purified more conveniently before crystallization from glacial acetic acid as follows. The hormone is precipitated by means of 99% alcohol as previously described and dissolved in water acidified with hydrochloric acid (Prepn. "B"). To this solution is added an excess of picric acid, which precipitates the active principle as described. The product is again just as active as the solution from which it was precipitated.

The active substance, whether it is prepared from the crystalline fraction or from preparation "B," is freed from picric acid and obtained in an extremely pure form by the following procedure. The picrate is dissolved in a small amount of glacial acetic acid. To this solution is added five times its volume of ethyl ether. The active material is precipitated as a brownish-yellow flocculent precipitate. It is centrifuged off and dissolved in distilled water, in which it now dissolves readily. The aqueous solution is adjusted to a *P*H of 5.4, whereupon the active substance again precipitates and is centrifuged off. The successive precipitation from acetic acid with ether and from aqueous solution at its isoelectric point is repeated several (4–5) times. The purified product finally comes down as a flesh colored flocculent precipitate which dries in clear, shiny amber plates with no definite structure. Table III gives the yield in milligrams from different kilogram samples and the guinea pig units contained in each sample.

TABLE III

ASSAY ON PURIFIED RELAXATIVE HORMONE

Sample	1	2	3	4	5	6
Yield per kg., C. L. tissue, mg.	35	30	17	21.5	43.5	32
G. P. units	1000	858	500	672	1230	914
Mg. of dried material per *G*. P. unit	0.035	0.035	0.034	0.032	0.034	0.035

The figures in Table III are selected to show the variation which may occur in different samples of tissue. The general yield which is ordinarily obtained varies from 850 to 1100 guinea pig units per kilogram of fresh tissue, but wider variations sometimes occur as shown in the table. Variation in the yield from a given amount of tissue is to be expected since no attempt is made to obtain corpora lutea only from pregnant or non-pregnant sows in the same stage of development. The more important fact, which is demonstrated in Table III, is that the amount of purified material representing a guinea pig unit is constant throughout.

The nitrogen content of the isolated material has been determined by Kemmerer's micro Kjeldahl method.[10,11] The samples were prepared by reprecipitation at the isoelectric point at least ten times, dried at 35° under atmospheric conditions, ground in an agate mortar and then dried at 60° in *vacuo*. The amount of nitrogen found in different preparations is constant as shown in Table IV.

TABLE IV

NITROGEN CONTENT OF PURIFIED MATERIAL

Sample	1	2	3	4	5	6	7	8
Nitrogen, %	11.52	11.78	11.55	11.24	11.55	11.49	10.78	11.38

Discussion

As to the chemical nature of relaxin, not much can be said conclusively at the present time. We believe that the purified product which we have obtained is at least a close approach to the pure substance and while we have not as yet obtained it in a pure crystalline form we may hope to do so. The product seems to act as a chemical individual toward all solvents and reagents to which we have subjected it. Its composition seems to be constant, if we may judge from the constant amount of nitrogen in every sample. As mentioned before, the product is amphoteric in nature and

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[10] G. Kemmerer and L. T. Hallett, Ind. *Eng.* Chem., 19, 1295 (1927).

[11] The authors are indebted to T. F. Setterquist for the analysis of the purified material.

has several other properties which would point to a peptide-like structure. However, with a nitrogen content of only 11% the chemical structure of the material appears to be different from typical peptides or polypeptides. The work which is reported in this paper lays the foundation for a more exact study of the chemical nature of the hormone.

Since insulin is generally considered to be peptide-like in nature, it is interesting to compare the two hormones, relaxin and insulin. Insulin is more definitely positive to protein reactions than is relaxin, but it can readily be seen that the two are very similar in a number of their properties.

TABLE V

COMPARISON OF THE PROPERTIES OF INSULIN AND RELAXIN

	Insulin	Relaxin
Isoelectric point	About P_H 5.0	P_H 5.4–5.5
Acid solution	Stable	Stable
Alkaline solution	Unstable	Unstable
Millon's reaction	Questionable	Negative
Biuret reaction	Positive	Questionable
Molisch Reaction	Negative	Negative
Picric acid	Precipitated by	Precipitated by
Trypsin	Destroyed	Destroyed
Pepsin	Destroyed	Destroyed

Summary

1. Methods for the extraction and purification of the relaxative hormone (Relaxin) are given.

2. The hormone has been obtained in a form in which it is associated with sodium chloride in relatively pure condition.

3. The hormone has also been concentrated to a highly purified form in which 0.035 mg. constitutes a guinea pig unit.

4. The chemical properties of the purified product are given. These are compared with those of insulin.

5. The name "Relaxin" is proposed to designate the relaxative hormone.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PRELIMINARY FORMATION OF ADDITION COMPOUNDS IN SUBSTITUTION REACTIONS OF AROMATIC TYPES. THE BROMINATION OF ETHYL 2-FURYLACRYLATE

BY HENRY GILMAN AND GEORGE F. WRIGHT

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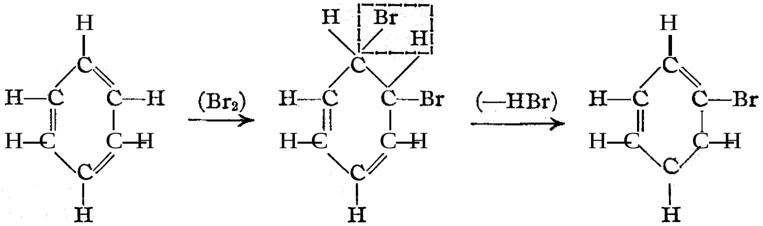
Introduction

Numerous explanations have been proposed to account for the mechanism of substitution reactions of aromatic compounds. Among these is that of Holleman,[1] postulating the formation of an intermediate addition compound which subsequently loses a hydrogen from the ring and a part of the addenda to give the ultimate substitution product. The following reaction may be taken by way of illustration of the bromination of benzene.



Two objections, in particular, have been raised against an interpretation of this kind. First, the preliminary addition compounds in such typical substitution reactions as halogenation, nitration, sulfonation, mercuration, arsonation, etc., have not been isolated. Second, if substitution did proceed via addition compounds, then such reactions should lead to the very ready formation of poly-substitution products, a conclusion which is not borne out by the readily controllable substitution reactions so characteristic of aromatic types. The expectancy of the facile formation of poly-substitution products appears reasonable to many in view of the fact that with the formation of the addition compound, the aromatic character is destroyed and the resulting dihydro-aromatic type should lend itself to the prompt formation of poly-addition compounds which in turn should yield poly-substitution products.

The first objection is not entirely valid. A part of it may be due to unfamiliarity with scattered references which may be proffered in support of preliminary addition. For example, the following observation[2] has

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[1] Holleman, "Die direkte Einführing von Substituenten in den Benzolkern," Leipzig, Veit and Co., 1910. In the illustration of the bromination of benzene, we might, of course, have 1,4-addition of bromine followed by 1,4-removal of hydrogen bromide.

[2] Muskat and Becker, THIS JOURNAL, 52,812 (1930). We must confess that we were unaware at first of all of the addition compounds referred to in our paper. It is certain that those which we have culled from a cursory examination of the literature are

just been made: "In studying the addition reactions of conjugated systems, we have a marked advantage over the study of similar reactions in the aromatic nucleus for it is possible to isolate the intermediate addition compound prior to its breakdown to the substitution derivative; in the reactions of aromatic compounds, only substitution products can as yet be isolated." The second objection has been tested recently by Van Alphen[3] and shown to lack validity, at least with Δ-2,6-dihydrophthalic acid.

The following references are pertinent to some of the illustration available in the literature which may be advanced in support of addition compounds being precursors of bromine substitution products: benzene,[4] naphthalene,[5] anthracene,[6] phenanthrene,[7] pyridine,[8] furan,[9] thiophene[10] and pyrrole.[11]

We are presenting at this time evidence for the preliminary addition of bromine to the furan nucleus incidental to the ultimate substitution of one of the nuclear hydrogens by bromine. It has long been known that some heterocyclic types like furan, thiophene and pyrrole have properties (physical, chemical and physiological[12]) which warrant their formal cor-

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far from being a complete list. A general account of addition preceding substitution may be found in Chapters IX and X of Johnson and Hahn's translation and enlargement of Henrich's "Theories of Organic Chemistry," Chapman and Hall, New York, 1922.

[3] Van Alphen, *Rec. trav. chim.*, 47, 169 (1928). This article contains references to related studies, and particularly to another type of addition (involving *one* and not two carbon atoms) proposed by Prins.

[4] Meunier, *Ann. chim. phys.*, [6] 10, 223 (1887). Mitscherlich, *Poggendorff's Ann. Phys. Chem.*, 35, 374 (1835).

[5] Laurent, *Ann. chim. phys.*, 59, 196 (1835); 66, 196 (1837); Orndorff and Moyer, *Am. Chem. J.*, 19, 262 (1897).

[6] Laurent, *Ann.*, 34, 295 (1840); Meyer and Jacobson, Vol. II, part 2, p. 516.

[7] Hayduck, ibid., 167, 177 (1873); Austin, *J. Chem. Soc.*, 93, 1760 (1908); Henstock, *ibid.*, 119, 55 (1921); 123, 3097 (1923). The prior formation of phenanthrene dibromide has been confirmed frequently by Dr. Arthur J. Hill.

[8] Hofmann, *Ber.*, 12, 988 (1879), and just recently Englert and McElvain, THIS JOURNAL, 51, 863 (1929). In these and related instances, it is definitely known that the bromine is initially attached to nitrogen. However, it is not definitely known whether the bromine subsequently adds to an ethylenic linkage.

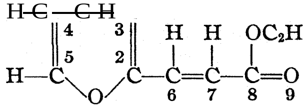
[9] Tonnies, *Ber.*, 11, 1086 (1878); Schiff and Tassinari, *ibid.*, 11, 842 (1878); Trefilev, *Ukrainskii Khem. Zhur.*, *1*, Sci. Pt., 121–296 (1925); [*C.A.*, 23, 3926 (1929)].

[10] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., New York, 1921, p. 36. This reference is to the general principle of preliminary addition. Very probably the initial step in bromination of sulfides at low temperatures is addition of the bromine molecule to sulfur. This is the case with diaryl sulfides [see Fries and Vogt, *Ann.*, 381, 337 (1911)].

[11] The problem of preliminary addition to the nitrogen in pyridine probably applies to pyrrole. Too little, however, is known about these very unstable bromopyrroles. (See Hess and Wissing, *Ber.*, 48, 1884 (1915).)

[12] Gilman and Pickens, THIS JOURNAL, 47, 245 (1925). Meyer and Jacobson, "Lehrbuch der Organischen Chemie," Vol. II, part 3, section I, pp. 12–17, contains a general critical account of the formulas of these compounds.

relation with benzene types. We have resolved a typical substitution reaction, the bromination of the furylacrylic nucleus, into two distinct steps: first, the addition of bromine to the ring, and then subsequent removal of hydrogen bromide. We previously demonstrated[13] that the substituted bromine occupies the 5-position.



This ethyl 5-bromofurylacrylate results definitely from a bromine addition compound, which subsequently loses hydrogen bromide. One atom of the bromine molecule[14] which added initially must have been attached to carbon 5. If addition occurred at one ethylenic linkage, then the other atom of bromine may have been on carbon 4, and this second atom of bromine subsequently combined with the hydrogen of carbon 5 to give hydrogen bromide and ethyl 5-bromofurylacrylate.

However, because of the multiple series of conjugated linkages in the ethyl furylacrylate, there are possibilities that the second bromine was attached (by 1,4-addition) to carbon 2 of the conjugated[15] system -(2,3,4,5); or (by 1,6-addition) to carbon 7 of the system -(7,6,2,3,4,5); or to oxygen 9 (by 1,8-addition) to the system -(9,8,7,6,2,3,4,5). This last we consider highly improbable.[16] A common interpretation would be addition to the 4,5-ethylenic linkage, although evidence with other reactions of the furan type under consideration makes it altogether likely that with some addenda we are dealing with 1,4- and with 1,6-additions. With 1,4-addition of bromine to the carbon atoms 2 and 5, it would only be necessary to have 1,4-removal of hydrogen bromide from carbon atoms 5 and 2. We are at present inclined to view the addition as 1,4-, partly because the second molecule of bromine apparently adds laterally to carbon atoms 6 and 7; because no ethyl 3- or 4-bromofurylacrylate has

[13] Gilman and Wright, *Rec. trav. chim.*, 49, 195 (1930).

[14] Possibly both bromine atoms may have been attached initially to carbon 5; see Ref. 3 of this paper.

[15] There are other theoretically possible conjugated systems, namely, those involving oxygen 1. If we assume that the oxygen is capable of functioning, latently or otherwise, in an oxonium form, then we have a hypothetical double bond emerging from this oxygen. and by virtue of such a condition, the conjugated systems -(1,5,4) and -(1,2,3) might be considered. However, neither of these would account (rearrangements excluded) for the attachment of bromine to carbon 5. In this connection, it is interesting to note that Moureu, Dufraisse and Johnson, *Ann. chim.*, 7, 8 (1927) have postulated prior addition of bromine to the oxygen in a study of furylacrylic acid. This will be considered in a later report on the more extensive bromination of furylacrylic acid and its ethyl ester.

[16] Kohler and Butler, THIS JOURNAL, 48, 1036 (1926); Lutz, *ibid.*, 51, 3008 (1929).

been isolated; and, finally, because polynuclear substitution takes place with great difficulty when the hydrogens attached to carbon atoms 2 and 5 have been replaced.

Experimental Part

The ethyl furylacrylate was prepared in accordance with the improved directions of Gilman, Brown and Jones.[17]

To **83** g. (0.5 mole) of ethyl furylacrylate in 200 cc. of dry carbon disulfide there was added dropwise and with constant stirring 80 g. (0.5 mole) of bromine in 50 cc. of carbon disulfide. One experiment was carried out at room temperature and another at −15°. The crystals which separated on chilling this solution to about −10° weighed 51 g., or 31% of the theoretical amount for the dibromide, and melted at 60°. When crystallized at a low temperature (—80 to 20") from petroleum ether (b. p. 40–Bo°), the compound melted at 70°. Because of the high instability of the dibromide, it was analyzed immediately.

Anal. Calcd. for $C_9H\,O_3Br_2$: Br, 49.08. Found: Br, 49.15.

The same compound was also prepared after the technique employed by Moureu, Dufraisse and Johnson[18] for the bromination of furylacrylic acid. To 41.5 g. (0.25 mole) of the ester in 100 cc. of chloroform was added slowly 40 g. (0.25 mole) of bromine. This reaction was carried out at −15° in an atmosphere of carbon dioxide which was circulated through a 500-cc. three-necked flask provided with a stirrer, dropping funnel and thermometer. When addition was completed, most of the solvent was removed at room temperature and under reduced pressure. The crystals which formed were separated by filtration and washed with a small quantity of petroleum ether. The yield of compound melting at 60° was 30 g. The compound was recrystallized from petroleum ether by dissolving it at room temperature and cooling to —80". The compound so obtained showed no depression in a mixed melting point determination with the dibromide prepared in carbon disulfide. During the crystallization about one-half of the original product did not dissolve in petroleum ether and this compound was identified as ethyl 5-bromo-2-furyl dibromopropionate, the acid of which was described previously by Gibson and Kahnweiler.[19] There appears to be less decomposition in the addition of bromine in a carbon disulfide solution.

When the dibromo addition compound was dissolved in alcohol and treated with zinc dust, the bromine atoms were removed and ethyl furylacrylate was obtained. The dibromo ester, dissolved in either chloroform or alcohol, appears to be unaffected by mercury.

A solution containing 6.5 g. (0.02 mole) of the dibromo ester in alcohol was treated with alcoholic potassium hydroxide until the mixture was alkaline. The potassium bromide (determined by silver bromide) obtained by filtration was 97.5% of the theoretical quantity. The filtrate was heated with dilute sodium hydroxide in order to hydrolyze the ester to the more readily workable acid. Acidification of this hydrolysate, subsequent to decolorization by Norite, yielded 5-bromofurylacrylic acid, which was identified by a mixed melting point determination with an authentic specimen.[13]

When the dry dibromo compound is permitted to decompose spontaneously (accompanied by the evolution of hydrogen bromide), very small quantities of 5-bromofurylacrylic acid can be isolated by the subsequent hydrolysis of the oil.

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[17] Gilman, Brown and Jones, *Iowa State Coll. J. of Science*, 2, 317 (1928).

[18] Moureu, Dufraisse and Johnson, *Ann. chim.*, 7, 8 (1927).

[19] Gibson and Kahnweiler, *Am. Chem. J.*, 12, 314 (1890).

Summary

When ethyl furylacrylate is treated with bromine, an unstable dibromo addition compound is formed which readily loses hydrogen bromide to give ethyl 5-bromofurylacrylate. The isolation and analysis of this intermediate dibromo compound is advanced as supplementary evidence for the prior formation of addition compounds in substitution reactions of aromatic types.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALBERTA]

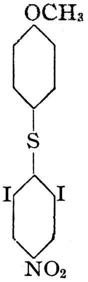
SOME DERIVATIVES OF DIPHENYL SULFIDE AND DIPHENYL ETHER

BY REUBEN B. SANDIN AND WRAY V. DRAKE

RECEIVED MAY 13, 1930 PUBLISHED AUGUST 5, 1930

The importance of the diaryl sulfide and diaryl oxide groupings in compounds which have therapeutic value has been demonstrated in the important work of T. B. Johnson[1] and C. R. Harington,[2] respectively. For this reason it was considered of interest to synthesize some sulfur ether analogs (Formula I) of 2,6-di-iodo-4-nitro-4′-methoxydiphenyl ether and its reduction compound 2,6-di-iodo-4-amino-4′-methoxydiphenyl ether. The latter compounds are intermediates in Harington and Barger's synthesis of thyroxine.[2] It was also considered of importance to prepare some oxygen ether isomers (Formulas II and III) of the above-mentioned compounds, *viz.*, 2,6-di-iodo-4-nitro-3′-methoxydiphenyl ether, 2,6-di-iodo-4-nitro-2'-methoxydiphenyl ether and the corresponding amino compounds.

The ultimate aim in view was to synthesize a sulfur ether analog of thyroxine[3] and also two oxygen ether isomers of thyroxine. Because this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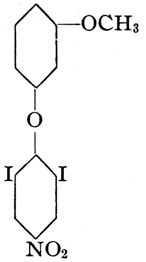
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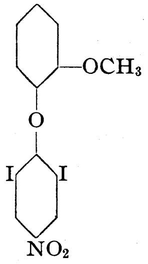
III

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[1] Hilbert and Johnson, THIS JOURNAL, 51, 1526 (1929); Bass and Johnson, *ibid.*, 52, 1146 (1930).

[2] Harington, Biochem. *J.*, 20, 293, 300 (1926); Harington and Barger, *ibid.*, 21, 169 (1927).

[3] This work is now in progress.

was a rather extensive field of investigation, and because of the departure of the junior author from this Laboratory, it was decided to report the work up to date.

In this work the authors have followed, in the main, the methods outlined by Harington and Barger.[2] The two isomers of hydroquinone monomethyl ether, *viz.*, guaiacol and resorcinol monomethyl ether, were condensed with 3,4,5-tri-iodonitrobenzene. The yields of the compounds produced, however, were much smaller than the yield of the corresponding hydroquinone monomethyl ether compound reported by Harington and Barger.[2] The yield in each case, which was really disappointing, apparently falls off as the methoxy group moves from position 4' to position 2'. The use of copper dust and longer periods of refluxing seemed to produce no beneficial results. The reduction of the nitro compounds to the amines was found to be a smooth reaction. For the purpose of identifying the amines, the acetyl derivatives and in some cases the benzoyl derivatives were prepared. The hydrochlorides of the amines were also prepared as a necessary step to subsequent diazotization.

The interaction of 3,4,5-tri-iodonitrobenzene and *p*-methoxythiophenol gave a fairly good yield of the sulfur ether compound. In fact, the yield was comparable to that of Harington's yield of 2,6-di-iodo-4-nitro-4′-methoxydiphenyl ether. Again the experimental conditions, with slight modifications, were those of Harington and Barger.[2] The sulfur ether compound was reduced, the amine acetylated and converted into the hydrochloride without difficulty.

Since these compounds have been prepared by standard methods, only the preparation of 2,6-di-iodo-4-nitro-4′-methoxydiphenyl sulfide will be described. The general properties, analytical data and some of the yields of these substances are given in the tables.

TABLE IA

DERIVATIVES OF DIPHENYL SULFIDE

No.	Compound	Solvent	Yield, %	Crystal form
1	2,6-Di-iodo-4-amino-4′-methoxy-	$(Et)_2O$	64	Gray-white needles
2	2,6-Di-iodo-4-acetylamino-4′-methoxy-	AcOH	Nearly quant.	Nearly colorless needles
3	Hydrochloride of 2,6-di-iodo-4-amino-4'-methoxy-	....	Nearly quant.	Colorless flakes

TABLE IB

DERIVATIVES OF DIPHENYL SULFIDE

No.	Formula	M. p., °C. (corr.)	Analyses				
			Calcd.		Found		
1	$C_{13}H_{11}ONSI_2$	172–173	I	52.5	I	52.4	52.6
2	$C_{15}H_{13}O_2NSI_2$	230	1	48.38	I	48.4	48.2
3	$C_{13}H_{12}ONSClI_2$	Decomp. 200	HCl	7.02	HCl	7.27	7.35

TABLE IIA

DERIVATIVES OF DIPHENYL ETHER

No.	Compound	Solvent	Yield, %	Crystal form
1	2,6-Di-iodo-4-nitro-2'-methoxy	Acetone or AcOH	25	Light gray needles
2	2,6-Di-iodo-4-nitro-3'-methoxy	AcOH	45–50	Yellow needles
3	2,6-Di-iodo-4-amino-2'-methoxy	Benzene	60	Light gray needles
4	2.6-Di-iodo-4-amino-3'-methoxy	$(Et)_2O$	60	Light pink needles
5	2,6-Di-iodo-4-acetylamino-2'-methoxy	AcOH	Nearly quant.	White needles
6	2,6-Di-iodo-4-acetylamino-3'-methoxy	Dil. AcOH	Nearly quant.	White needles
7	2,6-Di-iodo-4-benzoylamino-2'-methoxy	EtOH	......	White needles
8	2,6-Di-iodo-4-benzoylamino-3'-methoxy	EtOH	......	White needles
9	Hydrochloride of 2,6-di-iodo-4-amino-2'-methoxy	......	Nearly quant.	Gray-white flakes
10	Hydrochloride of 2,6-di-iodo-4-amino-3'-methoxy	......	Nearly quant.	Gray flakes

TABLE IIB

DERIVATIVES OF DIPHENYL ETHER

No.	Formula	M. p., °C. (corr.)	Analyses Calcd.		Analyses Found		
1	$C_{13}H_9O_4NI_2$	149–150	I	51.1	I	51.15	51.44
2	$C_{13}H_9O_4NI_2$	139–140	I	51.1	I	51.1	51.3
3	$C_{13}H_{11}O_2NI_2$	178–179	I	54.4	I	54.3	54.7
4	$C_{13}H_{11}O_2NI_2$	124–125	I	54.4	I	54.3	54.2
5	$C_{15}H_{13}O_3NI_2$	227–228	I	49.9	I	49.8	49.7
6	$C_{15}H_{13}O_3NI_2$	177–178	I	49.9	I	49.7	50.2
7	$C_{20}H_{15}O_3NI_2$	239–240	I	44.4	I	44.4	44.6
8	$C_{20}H_{15}O_3NI_2$	201–202	I	44.4	I	43.9	
9	$C_{13}H_{12}O_2NClI_2$	236–237 (decomp)	HCl	7.24	HCl	7.14	7.08
10	$C_{13}H_{12}O_2NClI_2$	132–134 (decomp.)	HCl	7.24	HCl	7.32	7.37

Experimental Part

2,6-Di-iodo-4-nitro-4'-methoxydiphenyl Sulfide, 111.—Fifty grams (0.1 mole) of 3,4,5-tri-iodo-nitrobenzene[2,4] and 14 g. (0.1 mole) of *p*-methoxythiophenol[5] were added to 250 cc. of boiling methyl ethyl ketone. To this mixture was added 30 g. of finely powdered, anhydrous potassium carbonate. After heating under a reflux condenser and in a current of hydrogen gas for five hours, the mixture was filtered. On cooling the filtrate, the bright yellow crystals of the pure nitro compound were obtained. On

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[4] Kalb, Schweizer, Zellner and Berthold, *Ber.*, 59, 1869 (1926).

[5] Prepared from p-anisidine by the method of Leuckart, *J. prakt. Chem.*, 41, 179 (1890)

evaporating the mother liquor the yield was increased. It was readily crystallized from acetone or methyl ethyl ketone. It melted at 138–139° (corr.) and the yield was **30** g. or 60%.

Anal. Calcd. for $C_{13}H_9O_3NSI_2$: I, 49.5. Found: I, 49.7, 49.2.

Summary

1. Some new derivatives of diphenyl sulfide and diphenyl ether have been prepared.
2. This work, with the possibility of leading to thyroxine-like compounds, is being continued.

EDMONTON, ALBERTA, CANADA

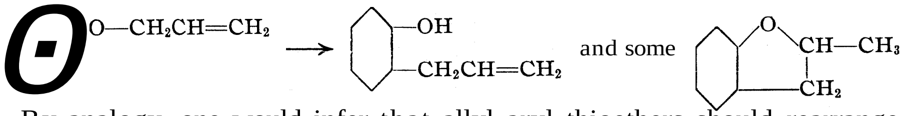
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PYROLYSIS OF ALLYL ARYL SULFIDES

BY CHARLES D. HURD AND HARRY GREENGARD

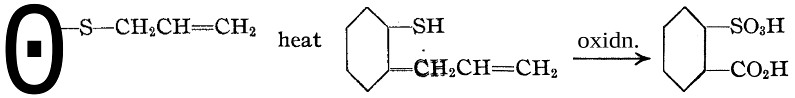
RECEIVED MAY 14, 1930 PUBLISHED AUGUST 5, 1930

The most striking property of allyl aryl ethers is their rearrangement[1] into o-allylphenols when they are heated. In some instances small yields of the isomeric methylcoumaranes have been observed as by-products. Allyl phenyl ether, for example, rearranges into o-allylphenol (80% yield) and 2-methylcoumarane (5% yield) by refluxing for six hours.



By analogy, one would infer that allyl aryl thioethers should rearrange similarly, if an ortho position is available, into *o*-allylthiophenols. Small amounts of dihydrothionaphthenes, the sulfur analogs of the coumaranes, might also be anticipated.

This problem has been approached by studying allyl phenyl sulfide and allyl *p*-tolyl sulfide, both of which were prepared in nearly quantitative yields from allyl bromide and the sodium salt of the aryl mercaptan. Allyl phenyl sulfide gradually undergoes rearrangement into o-allylthiophenol by refluxing, as witnessed by the increase in the boiling temperature during six hours from 207 to 240°. The o-allylthiophenol was identified by analysis of its lead salt, and by oxidation into o-sulfobenzoic acid



There is some evidence for the belief that a small amount of the hitherto undescribed 2-methyl-2,3-dihydrothionaphthene, A, was also formed during

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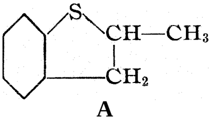
[1] For a survey of this topic, see Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc., New York, 1929, pp. 214–228.

the rearrangement. At least, a straw-colored liquid of higher boiling point than the original thioether and of lower boiling point than o-allylthiophenol was isolated which failed to form a salt with alcoholic lead acetate solution. The oxygen analog, 2-methylmumarane, also boils at a higher temperature than phenyl allyl ether and lower than o-allylphenol. It is interesting to note that o-allylthiophenol is insoluble in alkalies.



A

Allyl *p*-tolyl sulfide yielded 2-allyl-4-methylthiophenol by refluxing for several hours and as before, much of the original thioether was recovered.

Experimental Part

Allyl Phenyl Sulfide.—To an alcoholic solution (30 cc.) of sodium ethoxide (0.1 mole) was added 11 g. (0.1 mole) of thiophenol, followed by 13 g. (0.11 mole) of allyl bromide. There was an appreciable heat of reaction and an immediate precipitation of sodium bromide. The reaction completed itself by standing overnight, at which time it was no longer alkaline toward litmus. The alcohol and the excess of allyl bromide were distilled away on the water-bath, following which water was added to dissolve the sodium bromide. The upper oily layer was separated and the aqueous layer twice extracted with 25-cc. portions of ether. The combined product was dried over anhydrous calcium chloride, the ether removed and the residue vacuum-distilled. The yield was nearly quantitative (15 g.).

Phenyl allyl sulfide was found to have boiling points of 104–106° at 25 mm., and 215–218° at 750 mm. The refractive index, $n_{\mathrm{D}}^{20\ 5}$, was 1.4772. The thioether was inert toward an alcoholic solution of lead acetate, thus demonstrating the absence of a mercaptan group.

Effect of Prolonged **Refluxing.**—Twelve grams of phenyl allyl sulfide was refluxed on a fused salt bath in a small flask fitted with an upright air condenser and a thermometer immersed in the liquid. In the course of six hours the temperature rose from 207° to a maximum of 240°. The liquid darkened considerably. Also it acquired a pronounced mercaptan odor which was in decided contrast to the gasoline-like odor of the original thioether. By vacuum distillation, 8 g. of the original allyl phenyl sulfide was recovered and 3 g. of higher-boiling material was obtained. The constants for the latter were: b. p. 183–190° at 17 mm.; n_{D}^{21} 1.6098. This o-allylthiophenol had a decidedly unpleasant odor.

Lead Salt.—Although it was alkali insoluble, the liquid was considered to be *o*-allylthiophenol. To support this contention, the lead salt was precipitated metathetically by reaction of it with lead acetate, using alcohol as a common solvent. The heavy yellow precipitate which formed was washed with a little alcohol, then with dilute acetic acid, and dried in a desiccator. For analysis it was dissolved in dilute nitric acid and converted into lead sulfate in the usual way with sulfuric acid.

Anal. Subs., 0.2010, 0.2125: $PbSO_4$, 0.1206, 0.1284. Calcd. for $(C_9H_9S)_2Pb$: Pb, 41.0. Found: Pb, 41.0, 41.3.

Oxidation of **o-Allylthiophenol.**—In order to establish the structure of this substance, 1.5 g. of it was converted into o-sulfobenzoic acid by oxidation with a solution of 3 g. of potassium permanganate in 75 cc. of water. After two hours of refluxing, the precipitate of manganese dioxide was filtered off, the filtrate was concentrated to 40 cc., cooled and acidified. The white flocculent precipitate which appeared was purified by recrystallization from water; m. p. 66–67°. The pure trihydrate of o-sulfobenzoic acid, purified similarly, is known[2] to melt at 69°.

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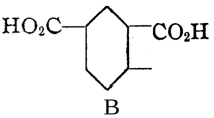
[2] Krannich, ***Ber.*, 33,** 3485 (1900).

Allyl *p*-Tolyl Sulfide.--This derivative of **thiocresol** was prepared in 97% yield by a method which was analogous to the one wherein thiophenol was used. Thus, 4.6 g. (0.2 mole) of sodium, 60 cc. of absolute alcohol and 25 g. (0.2 mole) of *p*-thiocresol (m. p. 44°) were admixed and caused to react with 25 g. (0.22 mole) of allyl bromide. The same vigorous reaction was noted but it was necessary to reflux the mixture for a short time to make it neutral to litmus. Upon working up as in the preceding case, there was obtained 32 g. of allyl *p*-tolyl sulfide, boiling at 123–127" and 25 mm.; n_{D}^{21} 1.5711.

2-Allyl-4-methylthiophenol.—When 11 g. of this thioether was refluxed for four hours, the temperature rose from 228 to 264°. By vacuum distillation, 5 g. of the thioether was recovered and 3 g. of yellow oil was collected at 190–196° and 11 mm.; n_{D}^{21} 1.6921. This allylthiocresol possessed a pronounced odor. There was a small amount of tarry residue.



B

A portion of the 2-allyl-4-methylthiophenol was oxidized as in the preceding experiment. A white solid subliming at 320" was isolated which is undoubtedly a sulfo-isophthalic acid of the structure shown (B). This compound is not described in the literature.

Lead Salt of 2-Allyl-4-methylthiophenol.—Part of the allylthiocresol was dissolved in alcohol and treated with alcoholic lead acetate solution. Heavy precipitation ensued. The precipitate, when first formed, was orange-colored and amorphous, but on standing for an hour it changed into light yellow needles which melted quite sharply at 330" with decomposition and formation of metallic lead.

Anal. Subs., 0.2100, 0.2236: $PbSO_4$, 0.1190, 0.1286. Calcd. for $(C_{10}H_{11}S)_2Pb$: Pb, **38.9.** Found: Pb, 38.7, 38.5.

2-Methyl-2,3-dihydrothionaphthene.—In order to ascertain the presence of a cyclic isomer of o-allylthiophenol, 8 g. of the purified rearrangement product, prepared from allyl phenyl sulfide as previously indicated, was treated with alcoholic lead acetate solution until precipitation was complete. The lead salt was filtered off and the alcohol removed from the filtrate by evaporation. The residue was then filtered from the excess of lead acetate and fractionated. In the lower-boiling fraction, about 0.2 g. of a straw-colored liquid was obtained at 103–108° and 8 mm. which yielded no precipitate with lead acetate and which unquestionably was different from o-allylthiophenol or the original thioether. Its refractive index was 1.5811, as compared with 1.4772 for the allyl phenyl sulfide and 1.6099 for o-allylthiophenol. Work is being continued on this subject.

Summary

A simple method of preparation has been given for allyl phenyl sulfide and for allyl *p*-tolyl sulfide. At the reflux temperature, the former undergoes a partial rearrangement into o-allylthiophenol. Small amounts of 2-methyl-2,3-dihydrothionaphthene are also produced. Similarly, allyl p-tolyl sulfide was found to pyrolyze into 2-allyl-4-methylthiophenol. The similarity in the pyrolysis of allyl aryl sulfides and of allyl aryl ethers is pointed out.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

AN APPARATUS FOR MICRO-CATALYTIC HYDROGENATION

BY J. F. HYDE AND H. W. SCHERP

RECEIVED MAY 15, 1930 PUBLISHED AUGUST 5, 1930

In the course of some work concerning the reduction of chlorophyll derivatives,[1] it became necessary to have a means of quantitatively measuring the amounts of gas absorbed by very small samples of material. The most desirable form of apparatus seemed to be either that devised by Barcroft,[2] or that devised by Warburg.[3] Both forms are used extensively by biologists for measuring reactions which involve small quantities of gases After a modified form of the Barcroft apparatus had been used with moderate success, the apparatus to be described was devised. It seems to be better adapted for chemical purposes than either of the other types mentioned, since it is equally accurate and is more easily manipulated. It is furthermore much less expensive than the present form of the Warburg apparatus.

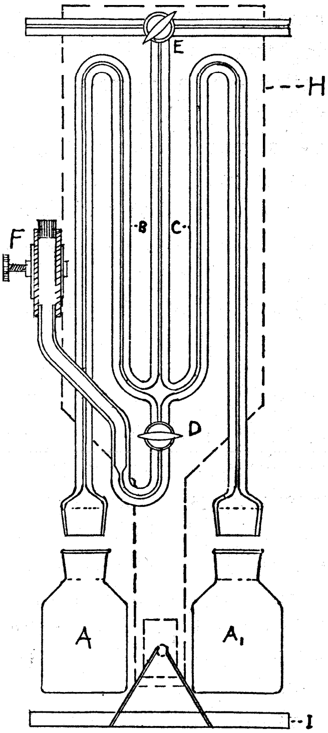


Fig 1.

The details of construction of the apparatus are shown in Fig. 1. It is most easily made from pyrex glass. The dimensions may be varied depending upon the size of samples with which one expects to be working. For reactions involving quantities of gas up to 0.04 millimole, the following size was found to be convenient. The bottles, A and A_1, are of sixty to seventy cubic centimeters' capacity. The manometer side arms are twenty centimeters in length and are made from one millimeter capillary tubing. The three way stopcock at E allows repeated evacuation and filling of the apparatus with the desired gas. The stopcock at D holds back the manometer liquid during evacuation and filling. The section of medium-sized glass tubing between F and D acts as a reservoir for the manometer liquid. F consists of a rubber tube closed at the upper end by a glass rod, and is fitted with a screw-clamp,

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[1] Conant and Hyde, THIS JOURNAL, 52, 1233 (1930).

[2] Barcroft and Haldane, *J. Physiol.*, 28, 233 (1902).

[3] Warburg, *Biochem. Z.*, 152, 51-63 (1924).

by means of which the liquid can be drained from the manometer or set at any level as in the Warburg apparatus. This arrangement makes it possible to take readings very rapidly. The glass apparatus is fastened to the wooden mounting H with a millimeter scale attached along the middle capillary tube. F is conveniently attached to either side of the mounting. The bottles A and A_1 are held in position by means of a small block of wood, I, which is placed under the bottles and held there firmly by passing under it a rubber band or wire spring, the ends of which are fastened to the wooden mounting. The latter is provided with a bearing near the center, by which it is supported on a shaft whose axis is perpendicular to the plane of the apparatus. Shaking is accomplished by means of a connecting arm attached to the mounting at a position near the top. The other end of the arm is fastened to a motor-driven eccentric. The shaft carrying the apparatus is clamped to a ringstand in such a way that it can be raised and lowered easily, since the bottles are to be immersed in a water-bath during the course of a reaction in order to keep both bottles at the same temperature. The sample tube G is made from ordinary six millimeter glass tubing about eight centimeters in length. A small bulb is blown on the end so that the glass is comparatively thin and can be broken at the proper time by shaking. With a little practice they are easily made so that premature breaking from the shaking of the apparatus at its usual speed (300–400 vibrations per minute) is avoided. The breaking of the tube at the desired time is made easier by inserting along with the sample a short pointed piece of glass rod. Before mounting the glass part it is necessary to measure as accurately as possible the volume in each side of the apparatus, including the bottles and the capillary up to the positions marked B and C in the manometer arms. This permits using the proper amounts of solvent in each bottle to make the remaining gas volumes equal to each other. The volume measurement is accomplished by filling with mercury and weighing.

The principle is the same as that involved in the use of the Warburg apparatus, namely, measuring the change in pressure at constant volume. The difference in pressure in the bottles A and A_1 is obtained by raising the level of the manometer liquid to the positions marked B and C successively, and each time noting the position of the meniscus in the central capillary tube. If these respective heights are designated h_B and h_C, the difference between the initial value of $h_B - h_C$ and the final value of h^1_B and h^1_C, after equilibrium has been established in the reaction, becomes a measure of the pressure change due to absorption of gas during the reaction. Since the filling in both sides of the apparatus is the same except for the sample, the one side serves as a blank.

The readings obtained as described are independent of any partial pressure effects, of the initial pressure, and of changes in atmospheric pressure. This can be shown in the following way. Let P and P_1 be the initial and final pressures, respectively, in a reaction involving n_C moles of gas. Suppose that the initial pressure had been P_2 instead, with the corresponding final pressure P_3. Since the temperature is assumed constant, we may write the following equation from the gas law,

$$\frac{P}{n} = \frac{P_1}{n_1} = \frac{P_2}{n_2} = \frac{P_3}{n_3} \tag{1}$$

where n, n_1, n_2, n_3 are the corresponding number of moles of gas present in the given volume.

Then

$$\frac{P - P_1}{n - n_1} = \frac{P_1}{n_1} = \frac{P_3}{n_3} = \frac{P_2 - P_3}{n_2 - n_3} \tag{2}$$

but by definition

$$n - n_1 = n_2 - n_3 = n_C \tag{3}$$

hence

$$P - P_1 = P_2 - P_3$$

The reading is, however, not independent of temperature changes. A simply constructed thermostat is suitable to use in measuring rates, but under ordinary circumstances, where it is desired to know only the total amount of gas absorbed, a few degrees' change in the temperature of the water-bath is negligible. The readings can be corrected for any temperature change if it is necessary, as is shown by the following calculations. Let P and P_1 be the initial and final readings at temperature T, and let P^1 and P^1_1 be the initial and final readings at a temperature T^1. Then, considering the volume as constant, the following equations can be written

$$\frac{P}{T} = \frac{P^1}{T^1} \quad \text{and} \quad \frac{P_1}{T} = \frac{P^1_1}{T^1}$$

Subtracting the second equation from the first, the following equations are obtained

$$\frac{P - P_1}{T} = \frac{P^1 - P^1_1}{T^1}, \text{ or}$$

$$p - P_1 = (P^1 - P'_1)\frac{T}{T^1} \tag{4}$$

The correction therefore involves multiplying the one reading by the ratio of the absolute temperatures.

The number of millimoles of gas equivalent to a change in pressure of one centimeter of the manometer liquid is calculated from the equation

$$n/cm = \frac{V \times 273 \times d}{T \times 22.4 \times 1033} \tag{5}$$

where V is the volume of gas, d is the density of the manometer liquid, and T is the average absolute temperature of the bath. If the same gas volume is used, n/cm will be always the same.

The substance is weighed into the sample tube, using a small glass tube as a funnel so that none of the material sticks to the part which will be heated. The sample tube is then drawn out to a thin capillary of such length and diameter that it will just about enter the capillary tube in the stopper of the reaction bottle, but is not sealed off. The bottles A and A_1 are then filled with the proper amounts of solvent and approximately two milligrams of platinum oxide catalyst, prepared in the manner described by Adams and Shriner.[4] The sample tube is placed in one of the bottles. The bottles are then placed in position and made fast after the ground joints are lightly greased. Excess grease is avoided, since it may dissolve in the solvent or the catalyst may stick to any exposed greasy surface. The apparatus is now evacuated four or five times with the stopcock D closed, each time refilling with hydrogen. It is very convenient to have one arm of the stopcock E connected throughout the run to a large bottle, which serves as a gas reservoir. The reservoir bottle is in turn attached by a siphon tube to another bottle so that as gas is used in sweeping out and filling the apparatus, it is displaced by water. The stopcock D is turned so that the apparatus and reservoir are connected. The apparatus is shaken for two to five minutes, during which time the platinum oxide is reduced. The shaking is now interrupted and the manometer liquid raised so that readings may be taken at B and C. The apparatus is now trapped off from the reservoir by the manometer liquid. The shaking is continued until after a ten or fifteen minute period the value of h_B-h_C is constant. This usually requires from half to three-quarters of an hour. At this point, if found desirable, the pressures may be readjusted by lowering the manometer liquid below the junction and raising it again. The apparatus is then removed from its shaft and the sample tube broken by a vigorous shake while holding it with the hands. With this accomplished the apparatus is replaced and the shaking continued. Readings are taken at frequent intervals until the pressure difference h_B-h_C becomes constant, indicating that equilibrium is again reached. In taking readings the shaking is interrupted by seizing the apparatus with one hand and adjusting the manometer levels with the other. The belt of the motor used for shaking is therefore adjusted so that it will slip with a little added resistance without jumping off. The product of the pressure change in centimeters multiplied by the calculated number of millimoles per centimeter is the number of millimoles of gas absorbed.

Table I contains some typical results for catalytic hydrogenation which show that an accuracy of $\pm 2\%$ is readily obtainable. In all these experiments the gas volume V was 68.4 cc. The manometer liquid was tetrachloro-ethane, density 1.58, and the temperature of the bath was 298°K. The corresponding value of n/cm was 0.0043 millimole. Glacial acetic acid was used as a solvent, 5 cc. being used in each experiment. In some cases the samples were weighed on a micro balance and in others aliquot portions of a solution of a larger sample were taken. The time required for the complete reduction of these substances was between thirty and sixty minutes.

TABLE I

EXPERIMENTAL DATA

Substance	Millimoles of sample	Change of pressure, cm.	Millimoles of H_2 absorbed
Maleic acid	0.0267	6.1	0.0263
Maleic acid	.0384	9.2	.0392
Dimethylacrylic acid	.0277	6.35	.0272
Dimethylacrylic acid	.0391	9.35	.0399
d-Pinene	.0394	9.6	.041
d-Pinene	.0394	9.35	.040

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[4] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

These results indicate that any possible sources of error such as a change in the state of saturation of the catalyst with the slight change in pressure may be neglected. In one or two instances the sample failed to be reduced, presumably on account of poisoning of the catalyst. This difficulty was largely eliminated by washing the reaction bottle thoroughly each time, rinsing with 10% potassium hydroxide solution and finally with distilled water.

The apparatus is not limited in use to hydrogenations. It has already been used with success in measuring the rate and extent of oxygen absorption of free radicals. In this work,[5] it has been found that using a 5-cc. sample of 0.01 M solution of free radical in tetrachloro-ethane at 25° and shaking at the rate of 400 vibrations per minute, absorption rates of oxygen having a half-time period as low as thirty-four seconds can be measured. The rate of solution of oxygen is great enough to maintain 90% saturation in the liquid phase under the stipulated conditions.

It has been suggested to us that this apparatus might be used for the measurement of vapor tension and its depression by solutes, photochemical and catalytic accelerations, equilibria in gas reactions involving liquids, solids or other gases and in bacteriological studies, such as those concerned with nitrogen-fixing bacteria.

Summary

1. An apparatus for the measurement of small quantities of gas absorbed or evolved in a chemical reaction has been described.

2. It is particularly adapted to catalytic hydrogenations on a microscale, in which case an accuracy of ±2% has been obtained under the conditions described.

CAMBRIDGE, MASSACHUSETTS

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[5] To be published by Conant and Scherp.

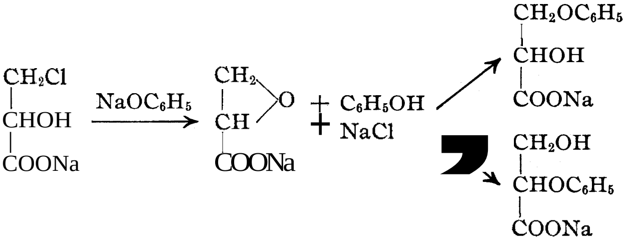
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE REACTION OF SODIUM PHENOXIDE WITH ALPHA-CHLOROHYDRACRYLIC ACID

BY C. FREDERICK KOELSCH

RECEIVED MAY 16, 1930 PUBLISHED AUGUST 5, 1930

In a recent paper[1] it was reported that the reaction between sodium phenoxide and β-chlorolactic acid led to the formation of a mixture of the two isomeric monophenyl ethers of glyceric acid, the amount of β-phenoxylactic acid isolated being some one hundred times greater than that of a-phenoxyhydracrylic acid. The occurrence of a-phenoxyhydrarylic acid was explained on the basis of the following formulation, involving the intermediate formation of glycidic acid



As was pointed out, it was possible that the β-chlorolactic acid used in the reaction was contaminated with a small quantity of a-chlorohydracrylic acid, and that the direct replacement of the chlorine in the latter compound gave rise to a-phenoxyhydracrylic acid; but since the reaction between a-chlorohydracrylic acid and ammonia had been reported[2] to yield only *iso*-serine, $CH_2NH_2CHOHCOOH$, it was argued that even if a-chlorohydracrylic acid were present, it would react with sodium phenoxide to give glycidic acid, which would then add phenol, forming a mixture of monophenylated glyceric acids. Since the addition of phenol to glycidic acid could take place in two different ways, two isomers would be formed in a ratio dependent on factors which are discussed by Michael[3] in his "Partition Principle." The positions of the phenoxyl and hydroxyl in the product would thus be independent of the positions of the chlorine and hydroxyl in the reactant containing these.

Such reasoning, based on analogy, might easily lead to false conclusions. Accordingly, it was deemed advisable to verify the statement that a-chlorohydracrylic acid and sodium phenoxide would react to form mainly β-phenoxylactic acid. The results obtained, which are the subject of this paper, are in complete accord with the prediction.

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[1] Koelsch, THIS JOURNAL, 52, 2430 (1930).

[2] Melikoff, *Ber.*, 13, 1265 (1880).

[3] Michael. *J. prakt. Chem.*, [2] 60,290 (1899).

The α-chlorohydracrylic acid taken was prepared by a method similar to that used for the preparation of the corresponding bromo acid[4] by the action of silver carbonate on α,β-dichloropropionic acid. Although it was obtained as a non-volatile, uncrystallizable sirup, it was shown to be reasonably pure by analysis. That it was quite free from β-chlorolactic acid was shown by dehydration to form a-chloro-acrylic acid which crystallized in needles that melted at 65°.[5] The dehydration of β-chlorolactic acid would be expected to give β-chloro-acrylic acid which crystallizes in plates that melt at 84°.[6] The formation of the latter acid was not observed.

α,β-Dichloropropionic Acid.?—A mixture of 50 g. of red fuming nitric acid (d. 1.5) with 100 g. of nitric acid (d. 1.4) was added to 50 g. of glycerol α,β-dichlorohydrin;[8] the temperature was kept below 15" during the addition by external cooling. The mixture was then allowed to come to room temperature, when a vigorous reaction set in. After the mixture had stood overnight, it was distilled under reduced pressure. The part boiling above 100" (15 mm.) was redistilled, giving 38 g. boiling at 112–115" (12 mm.), which soon solidified to a mass of colorless needles melting at 47–50".

a-Chlorohydracrylic Acid.—A solution of 37 g. of silver nitrate was treated with a slight excess of sodium carbonate (32 g. of $Na_2CO_3 + 10H_2O$) solution. The silver carbonate was washed repeatedly by decantation, suspended in 100 ml. of water, and added to a solution of 30 g. of α,β-dichloropropionic acid in 50 ml. of water. The mixture was heated on a steam-bath for two hours and then filtered. Since the filtrate still contained silver, the heating was continued for two hours. The solution, then free from silver, was filtered and evaporated to a sirup on a steam-bath. After standing for three days in a vacuum desiccator over sulfuric acid and sodium hydroxide, the product was analyzed; yield, 16.5 g.

Anal. Subs., 0.1862: AgCl, 0.1988. Calcd. for $C_3H_5O_3Cl$: Cl, 28.44. Found: Cl, 26.42.

a-Chloro-acrylic Acid.—To a mixture of 2.5 ml. of sulfuric acid (d. 1.84) with an equal volume of water was added 1.0 g. of a-chlorohydracrylic acid. The mixture was refluxed for one hour, cooled, diluted with 7 ml. of water, filtered from carbonaceous material, and extracted with five 2-ml. portions of alcohol-free ether. The ether was evaporated from the combined extracts, and the brown residue, which was almost completely crystalline, was purified by slow sublimation at 10 mm. The product formed colorless monoclinic prisms melting at 64–66°; yield, 0.3 g.

β-Phenoxylactic and a-Phenoxyhydracrylic Acids from **α-Chlorohydracrylic** Acid.—To a mixture of 15 g. of phenol with 10 g. of a-chlorohydracrylic acid and 20 ml. of water was added a solution of 9 g. of sodium hydroxide in 30 ml. of water. The mixture was refluxed for thirty minutes, acidified with hydrochloric acid, and steam distilled until a test with ferric chloride showed the absence of phenol from the distillate. The separation of a-phenoxyhydracrylic and β-phenoxylactic acids was carried out as described previously.'

After recrystallization from water there was obtained 4.6 g. of β-phenoxylactic

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[4] Neuberg and Mayer, *Biochem. Z.*, *3*, 119 (1907).

[5] Otto and Beckurts, *Ber.*, 18, 242 (1885).

[6] Otto, *Ann.*, 239, 270 (1887).

[7] Cf. Henry, *Ber.*, 7, 414 (1874).

[8] Prepared according to the directions of King and Pyman, *J. Chem. Soc.*, *105*, 1257 (1914).

acid which crystallized in plates that melted at 157–159°. The anilide prepared from this acid, after crystallization from alcohol and from water, melted at 122–123°.

The α-phenoxyhydracrylic acid obtained was purified by crystallization from toluene and from water, the usual crystallization from chloroform being omitted because of the small quantity in hand; the product formed needles melting at 102–106°; yield, 0.083 g. A mixture with an equal amount of the pure acid (m. p. 109–110°) melted at 103–106°.

The assistance of Professor S. M. McElvain is gratefully acknowledged.

Summary

The reaction between sodium phenoxide and α-chlorohydracrylic acid is shown to yield a mixture of α-phenoxyhydracrylic acid and β-phenoxylactic acid in which the latter predominates greatly.

This is in agreement with the prediction based on the behavior of α-chlorohydracrylic acid toward ammonia and indicates that the α-phenoxyhydracrylic acid formed in the reaction between sodium phenoxide and β-chlorolactic acid does not owe its origin to the presence of α-chlorohydracrylic acid as an impurity in the β-chlorolactic acid.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE DETERMINATION OF THE PURITY OF ACETIC ANHYDRIDE

BY CHESTER K. ROSENBAUM AND JAMES H. WALTON

RECEIVED MAY 19, 1930 PUBLISHED AUGUST 5, 1930

Introduction

A rapid and accurate method for the quantitative determination of acetic anhydride is of great practical importance because of the extensive industrial uses of this reagent. In a publication by Whitford[1] and the senior author of this paper it was shown that anhydrous oxalic acid is decomposed quantitatively in the presence of pyridine, acting as a catalyst, according to the equation

$$(COOH)_2 + (CH_3CO)_2O = CO_2 + CO + 2CH_3COOH$$

This reaction had been reported by Dr. Schierz[2] of this Laboratory, who observed that various tertiary bases such as picolines, butidine, collidine, etc., could also be used as catalysts. Whitford found that the pyridine acts as a catalyst for the reaction through the formation of pyridine acid oxalate $C_5H_5N{\cdot}(COOH)_2$ which is subsequently decomposed by the acetic anhydride.

The carbon dioxide and carbon monoxide evolved in the reaction were measured by Whitford to give a gasometric method for the determination of acetic anhydride. He found his method to be accurate to within 0.1%

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[1] Whitford and Walton, THIS JOURNAL, 47, 2934, 2939 (1925).

[2] Schierz, *ibid.*, 45, 455 (1923).

for samples of pure acetic anhydride and also for 92% acetic anhydride. In the present investigation the same reaction was used but instead of measuring the gases evolved, the excess oxalic acid was determined by a potassium permanganate titration.

Procedure

About one gram of different samples of acetic anhydride was weighed from a weighing pipet into a wide-mouthed glass-stoppered bottle containing about one gram of anhydrous oxalic acid prepared by the method of Hultman, Davis and Clark.[3] Two cc. of pyridine dried over barium oxide and calcium hydride was then added and the bottle kept cool in water for five minutes to prevent vaporization of the acetic anhydride. After standing for ten minutes longer at about 50°, the excess oxalic acid was titrated with $N/10$ potassium permanganate. The results were checked by the standard alkalimetric titration carried out as follows.

About *170* cc. of ***0.1351*** N sodium hydroxide was measured from a buret into a flask and about one gram of acetic anhydride was then weighed into the sodium hydroxide solution from a weighing pipet. The anhydride was allowed to hydrolyze at 40° for eight hours and the excess sodium hydroxide then titrated with $N/10$ hydrochloric acid. The results were calculated by the method described by Scott.[4]

RESULTS

Sample	Percentage of acetic anhydride $(COOH)_2$ method	 NaOH titration
A	*79.01*	*79.15*
B	86.52	86.2
C	*92.19*	*91.7*

Notes.—All materials were tested for oxidizing and reducing substances and if any were present, a blank was run. Other acids or acid-forming materials in the acetic anhydride did not affect the oxalic acid method but did give high results when an alkalimetric titration was run with certain samples of commercial anhydride. In an alkalimetric titration of a one-gram sample, the presence of 0.2% of acetyl chloride will raise the calculated percentage of acetic anhydride by 1%. The presence of small amounts of acetyl chloride, however, does not affect the oxalic acid method. Similarly an error of only 0.1 cc. of $N/10$ sodium hydroxide will change the calculated percentage of acetic anhydride by about **0.4%**. The other standard methods[5] are more accurate than an alkalimetric titration but require considerable time and care.

The purity of the anhydrous oxalic acid used in this investigation was found to be **99.84%** by a potassium permanganate titration. The presence of a small percentage of water in the oxalic acid apparently does not vitiate the results, as is evidenced by the fact that **99.69%** pure anhydrous oxalic acid when used gave correct values. This is explained by the fact

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[3] Hultman, Davis and Clark, THIS JOURNAL, *43,366 (1921).*

[4] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, New York, 1922, Vol. II, p. *1054.*

[5] See Radcliffe and Medofski, *J. Soc. Chem. Ind., 36,628 (1917).*

that the reaction between oxalic acid and acetic anhydride is so rapid that the water does not have opportunity to react with the anhydride. The only considerable error that can be introduced was found to be a lowering of the results caused by the vaporization of the anhydride due to the heating when pyridine was added. This error varied from 0.2 to 0.5% but is avoided by cooling the container. The amount of pyridine added was varied from 1 to 5 cc. with no effect on the results. An error of 0.1 cc. in the potassium permanganate titration causes a deviation of only 0.05%.

Summary

A method has been devised for the determination of the purity of acetic anhydride based on the decomposition of anhydrous oxalic acid by acetic anhydride using pyridine as a catalyst, and subsequently determining the excess oxalic acid with potassium permanganate. The method is simple, rapid and easily accurate to within 0.1%.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SYMMETRICAL DIALKYL-TETRA-TERTIARY-BUTYLETHINYL-ETHANES

BY H. B. GILLESPIE AND C. S. MARVEL

RECEIVED MAY 19, 1930 PUBLISHED AUGUST 5, 1930

Recent work by Ziegler and Schnell[1] and by Conant and his students[2] has indicated that certain dialkyl-tetra-arylethanes have properties that resemble quite closely those of the hexa-arylethanes. In particular, it has been found that a tertiary butyl group or a cyclohexyl group can replace a phenyl group without greatly changing the amount of dissociation of the ethane. Work in this Laboratory on the acetylenic ethanes has shown that hexa-*tert.*-butylethinylethane[3] (I) is cleaved by 1% sodium amalgam and resembles in this respect the hexa-arylethanes. Rossander and Marvel[4] have observed that diphenyl-tetra-*tert.*-butylethinylethane (II) requires 40% sodium amalgam for cleavage and hence is more stable toward alkali metals than is the hexa-acetylenic compound. The series of tetra-acetylenic ethanes has now been extended to include di-*tert.*-butyl-tetra-*tert.*-butylethinylethane (III) and dicyclohexyl-tetra-*tert.*-butylethinylethane (IV).

$$[(CH_3)_3C{-}C{\equiv}C]_3{-}C{-}C[C{\equiv}C{-}C(CH_3)_3]_3$$

I

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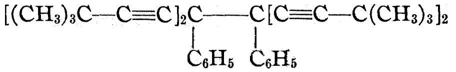
[1] Ziegler and Schnell, Ann., 437, 252 (1924).

[2] Conant and Small, THIS JOURNAL, 47, 3068 (1925); Conant, Small and Sloan, *ibid.*, 48, 1743 (1926); Conant and Bigelow, ibid., 50, 2041 (1928).

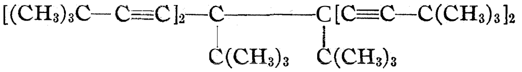
[3] Salzberg with Marvel, *ibid.*, 50, 1737 (1928).

[4] Rossander and Marvel, *ibid.*, 51, 932 (1929).



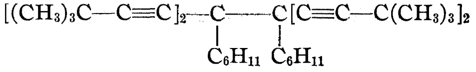
$$[(CH_3)_3C{-}C{\equiv}C]_2\underset{C_6H_5}{C}{-}\underset{C_6H_5}{C}[C{\equiv}C{-}C(CH_3)_3]_2$$

II



$$[(CH_3)_3C{-}C{\equiv}C]_2{-}\underset{C(CH_3)_3}{C}{-}\underset{C(CH_3)_3}{C}[C{\equiv}C{-}C(CH_3)_3]_2$$

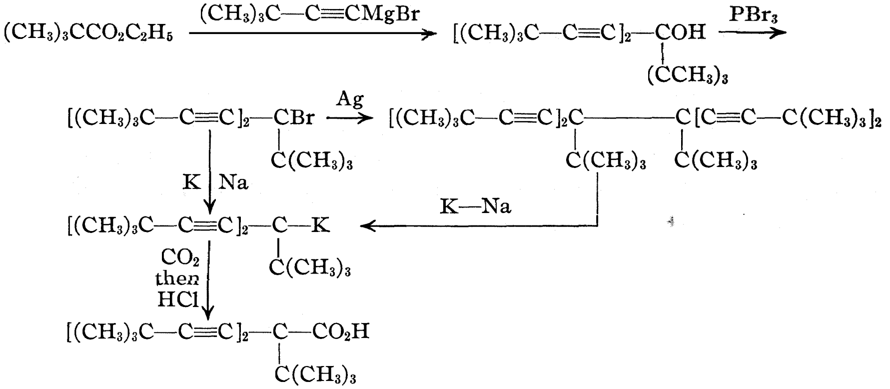
III



$$[(CH_3)_3C{-}C{\equiv}C]_2{-}\underset{C_6H_{11}}{C}{-}\underset{C_6H_{11}}{C}[C{\equiv}C{-}C(CH_3)_3]_2$$

IV

Di-*tert.*-butyl-tetra-*tert.*-butylethinylethane (III) was prepared by a series of reactions starting with ethyl trimethylacetate and *tert.*-butylethinylmagnesium bromide. The steps in the synthesis and structure proof are indicated



This ethane was found to be more stable than the corresponding diphenyl derivative (II) since cleavage could be accomplished only by use of liquid sodium–potassium alloy. The ethane was stable toward heat at 140°, since it could be recovered unchanged after boiling the xylene solution. It did not absorb oxygen when dissolved in *p*-dibromobenzene and heated to 140°.

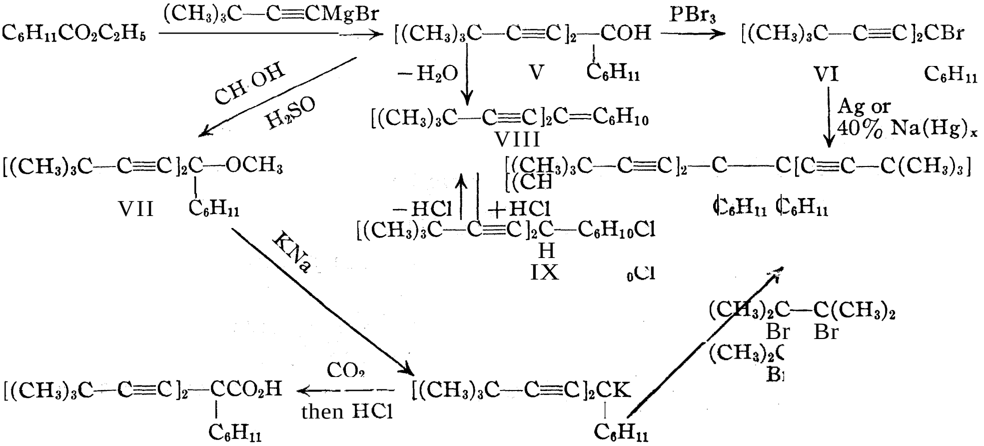
Dicyclohexyl-tetra-*tert.*-butylethinylethane was prepared from ethyl hexahydrobenzoate by much the same method that had been used for the tertiary butyl derivative. Cyclohexyl-di-*tert.*-butylethinylbromomethane (VI) did not react readily with silver although a low yield of a hydrocarbon was obtained. Then several other methods of preparation were studied. When the bromide was treated with 40% sodium amalgam, very little metal alkyl was obtained, but the same hydrocarbon was formed. This hydrocarbon was not cleaved by liquid sodium–potassium alloy. Some metal alkyl was obtained by the action of liquid sodium–potassium alloy[6] on the methyl ether of cyclohexyl-di-*tert.*-butylethinylcarbinol (VII).

[5] Ziegler and Schnell, Ann., 437,227 (1927).

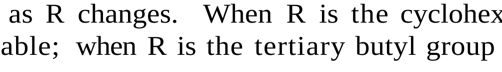
From this derivative the acid was obtained by the action of carbon dioxide. With tetramethylethylene dibromide the metal alkyl gave the same hydrocarbon that had been obtained previously by the action of silver on the bromide.

Since this hydrocarbon was not cleaved by alkali metals its structure has not been established beyond question. However, the fact that it has been obtained by so many different methods seemed to leave little doubt concerning its structure. An attempt was made to prepare the isomeric hydrocarbon which would have formed if the carbinol (V) had teen dehydrated and then halogen acid had added to the double bond to give an isomeric halogen derivative of the structure represented in formula IX. The carbinol (V) was dehydrated to give di-*tert.*-butylethinylcyclohexylidenemethane (VIII) and hydrogen chloride was added to the olefin in alcohol solution. The chloride was oily and was never obtained in a pure condition. When this crude chloride was treated with 40% sodium amalgam, no evidence of metal alkyl formation was found. The only hydrocarbon that could be isolated from this reaction mixture was the original olefin. This behavior of the isomeric chloride furnished additional evidence that the hydrocarbon obtained from the true chloride of cyclohexyl-di-*tert.*-butylethinylcarbinol is the desired dicyclohexyltetra-*tert.*-butylethinylethane.

These reactions are represented graphically as follows



It is interesting to note the variation in the ease of cleavage of the compounds of the general formula



$$[(CH_3)_3\text{—}C\text{—}C\equiv C]_2\text{—}\underset{R}{\underset{|}{C}}\text{—}\underset{R}{\underset{|}{C}}\text{—}[C\equiv C\text{—}C(CH_3)_3]_2$$

with alkali metals as R changes. When R is the cyclohexyl group the molecule is very stable; when R is the tertiary butyl group the molecule is cleaved by liquid sodium–potassium alloy; when R is the phenyl group the molecule is cleaved by 40% sodium amalgam; and when R is the *tert.*-butylethinyl group the molecule is cleaved by 1% sodium amalgam. The stability of the cyclohexyl derivative is particularly surprising in view of the ease with which tetracyclohexyldiphenylethane reacts with 1% sodium amalgam to give a metal alkyl.[6]

Experimental Part

Tert.-butyl-di-*tert.*-**butylethinylcarbinol.**—Tert.-butylethinylmagnesium bromide was prepared by adding 35 g. of *tert.*-butylacetylene from a dropping funnel to 108 cc. of a 3.945 N ether solution of ethylmagnesium bromide during four hours. The heat of reaction was sufficient to cause the ether to reflux and an efficient condenser filled with water at about 5° was needed to avoid loss of acetylene. Half of the theoretical amount (13.4 g.) of ethyl trimethylacetate was then added during three to four hours and the mixture was stirred overnight. The remainder of the ester (13.4 g.) was added during four hours. The mixture was stirred for about three hours longer and then decomposed by pouring it on cracked ice and 25 g. of ammonium chloride and then adding the theoretical quantity of dilute hydrochloric acid. The ether layer after being dried over anhydrous magnesium sulfate was heated on the steam-bath to remove the solvent. The residue was distilled under diminished pressure and the fraction boiling at 95–99° at 5 mm. or 103–107° at 7 mm. was collected. This distillate solidified on standing to give white rhombic crystals; m. p. 46–47". The yield was 4042 g. (78–82% of the theoretical amount).

Anal. Subs., 0.2429: CO_2, 0 7322; H_2O, 0 2487. Calcd. for $C_{17}H_{28}O$: C, 82.19; H, 11.37. Found: C, 82.20; H, 11.46.

Tert.-**butyl-di-*tert.*-butylethinylbromomethane.**—Three grams of the carbinol was dissolved in 25 cc. of low-boiling petroleum ether and the solution was cooled to 0°. Then 1 g. of phosphorus tribromide was added and the solution stirred at 0° for one hour. To the mixture was slowly added 100 cc. of 10% sodium bicarbonate solution and stirring was continued for ten minutes. The ether layer, after being dried over anhydrous magnesium sulfate, was evaporated under reduced pressure. The bromide appeared as a viscous yellow oil. All attempts to crystallize it failed The yield of crude product was 2.4–2.6 g. (63–69% of the theoretical amount). This crude bromide was s ~ & -ciently pure for the preparation of the ethane.

One run of the bromide was distilled under reduced pressure and the fraction boiling at 68–71▪ at 13 mm. was collected.

Anal. (Stepanow). Subs., 0.1482: 11 19 cc. of 0.4387 N $AgNO_3$. Calcd. for $C_{17}H_{27}Br$: Br, 25.69. Found: Br, 26.12.

Sym.-**di-*tert.*-butyl-tetra-*tert.*-butylethinylethane.**—The crude *tert.*-butyl-di-*tert.*-butylethinylbromomethane obtained from 3 g of carbinol was dissolved in 10 cc. of dry ether and shaken mechanically with 3 g. of molecular silver for twenty-four hours. The ether solution was evaporated under reduced pressure almost to dryness and 5 cc. of absolute alcohol was added. The evaporation was continued until crystallization began and then the mixture was cooled. The yield was 0.87 g. (31.6% of the theoretical amount); m. p. 120–120.5°.

Anal. Subs., 0.1942: CO_2, 0.6267; H_2O, 0.2042. Calcd. for $C_{34}H_{54}$: C, 88.23; H, 11.76. Found: C, 88 00; H, 11.77. Mol. wt. (Cryoscopic in benzene). Subs , 0.0901, 0.2421; benzene, 13.1765; Δ^t, 0.086, 0.208". Calcd. for $C_{34}H_{54}$: mol. wt., 462. Found: 452, 449.3.

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[6] Rossander, Bock and Marvel, THIS JOURNAL, 52, 2976 (1930).

Cleavage of the Ethane with Alkali Metals.—A solution of 0.1 g. of ethane in 10 cc. of dry ether was shaken with 2 cc. of liquid sodium–potassium alloy in an atmosphere of **dry** nitrogen. The solution instantly became yellow in color and a deep red color developed within one to two minutes. The isolation of the *tert.*-butyl-di-*tert.*-butylethinylacetic acid is described below.

When 0.1 g. of ethane was shaken for twenty-four hours with 4–5 cc. of 40% sodium amalgam under the conditions described above, no red coloration appeared and most of the ethane was recovered.

A solution of 0.5 g. of the bromide in dry ether was shaken for twenty-four hours with 4–5 cc. of 40% sodium amalgam in an atmosphere of nitrogen. No red color developed and no acid was formed upon treating the reaction mixture with carbon dioxide and mineral acid. From the ether of the reaction there was obtained 0.05 g. of the ethane melting at 119–120°.

Tert.-**butyl-di-*tert.*-butylethinylacetic** Acid. (A) From **Di-*tert.*-butyl-tetra-*tert.*-butylethinylethane.**—One gram of ethane was shaken for twenty-four hours with 4–5 cc. of liquid sodium–potassium alloy in ether. Dry carbon dioxide was then passed into the reaction mixture until the red color disappeared. The ether and acid salt were decanted from the excess alloy and carefully treated with a little absolute alcohol to decompose any small particles of the alloy, then with water and finally with dilute hydrochloric acid. The ether layer was extracted with a solution of 2.5 g. of potassium hydroxide in 50 cc. of water. The alkaline layer was cooled to 0° and acidified. The brown oil which separated was extracted with ether and the ether solution was dried over anhydrous magnesium sulfate. The ether was then evaporated at room temperature. The oil was shaken up in a little hot glacial acetic acid and filtered. The crystals which separated on cooling the filtrate were again recrystallized from glacial acetic acid. The yield was 0.426 g. (35.7% of the theoretical amount); m. p. 151.5–152.5°. This acid caused no depression of the melting point when mixed with a sample of the acid prepared from the bromide.

(B) From *Tert.*-**butyl-di-*tert.*-butylethinylbromomethane.**—The crude bromide obtained from 6 g. of carbinol was dissolved in 20 cc. of dry ether and shaken with a large excess (8–10 cc.) of liquid sodium–potassium alloy for twenty-four hours in an atmosphere of dry nitrogen. Dry carbon dioxide was then passed into the reaction mixture until the red color disappeared. The ether and acid salt were then treated as described above with a little absolute alcohol and then with water. The ether layer was separated and thoroughly extracted with water. The extracts were added to the main aqueous layer, which was then cooled to 0° and acidified. The red gum which separated was extracted with ether and reprecipitated by extracting the ether solution with a solution of 5 g. of potassium hydroxide in 50 cc. of water and acidifying the alkaline extract. The gum was then isolated as described above and recrystallized several times from glacial acetic acid. The yield of pure acid was 0.75 g. (11.2% of the theoretical amount); m. p. 152.5–153.5°.

Anal. Subs., 0.2007: CO_2, 0.5781; H_2O, 0.1860. Calcd. for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.53; H, 10.37. Neutral equivalent. Subs., 0.1069: 3.35 cc. of 0.1153 N NaOH. Calcd. for $C_{18}H_{28}O_2$: 276.3. Found: 276.7.

In one run similar to the one described above, not enough of the alloy was used to provide a large excess. In this case a few white crystals were isolated from the ether of the reaction mixture after its separation from the aqueous solution. After recrystallization from ether and alcohol these melted at 170–173.5'. This was probably a rearranged hydrocarbon but not enough was isolated for further identification. Conant and Bigelow[2] observed a similar production of a rearranged hydrocarbon when diphenyl-*tert.*-butylchloromethane was shaken with an insufficient quantity of liquid sodium–potassium alloy.

Effect of Heat on the Ethane.—A solution of 0.1 g. of ethane in 4 cc. of absolute alcohol was heated in a sealed tube at 100° for one hour. No color was developed. Upon concentrating the alcoholic solution and cooling to 0°, 0.07 g. of ethane was recovered (m. p. 120.5').

A solution of 0.1 g. of ethane in 3 cc. of dry xylene was heated in a sealed tube to 140° for one hour. No color developed and 0.05 g. of ethane was recovered (m. p. 120.5°).

Oxygen Absorption.—Seven hundredths of a gram of di-*tert.*-butyl-tetra-*tert.*-butylethinylethane was placed in a 50-cc. Florence flask and 5 g. of p-dibromobenzene was added. The flask was then placed in an oil-bath at 140° and connected to a eudiometer filled with oxygen. The same temperature was maintained for one and one-half hours but no absorption of oxygen was observed.

Cyclohexyl-di-*tert.*-butylethinylcarbinol.—The same procedure was followed in the preparation of this carbinol as described under *tert.*-butyl-di-*tert.*-butylethinylcarbinol. The *tert.*-butylethinylmagnesium bromide was made from 24 g. of *tert.*-butylacetylene and 93.5 cc. of a 3.12 N ether solution of ethylmagnesium bromide. To the acetylenic Grignard reagent was added 22.5 g. of ethyl hexahydrobenzoate. The carbinol was isolated and distilled under diminished pressure, collecting the material boiling at 123–128" at 3 mm. The yield was 28 g. (70% of the theoretical amount). It had the following constants: sp. gr. $^{20}_{20}$, 0.8991; n^{20}_{D} 1.4729. Calcd. for $C_{19}H_{30}O$: M_D, 85.42. Found: M_D, 85.47.

Anal. Subs., 0.2294: CO_2, 0.6984; H_2O, 0.2202. Calcd. for $C_{19}H_{30}O$: C, 83.21; H, 10.95. Found: C, 82.02; H, 10.74.

In a small side-arm test-tube (25 cc.) was placed 0.293 g. of pure carbinol dissolved in a few cc. of dry benzene. The side arm was connected to an outfit for drying and collecting ethane gas. An excess of ethylmagnesium bromide was added to the carbinol from a dropping funnel, and 25 cc. of ethane at S. T. P. was collected. The theoretical yield of ethane is 23.9 cc.

The carbinol was further characterized by converting it to a solid acetate.

Cyclohexyl-di-*tert.*-butylethinylmethyl Acetate.—One and one-half grams of the carbinol was added to a suspension of I g. of powdered potassium in petroleum ether (b. p, 40–60°) and stirred for about ten minutes. The supernatant liquid was decanted and treated with 2 cc. of acetic anhydride with stirring. The mixture was decomposed with water and neutralized with sodium bicarbonate solution. The ether layer was separated, dried with magnesium sulfate and concentrated to 3 4 cc. under diminished pressure. On cooling, the ester crystallized. The yield was 0.5 g.; m. p. 91–93". Recrystallization from acetone raised the melting point to 95–96°.

Anal. Subs., 0.1725: CO_2, 0.5018; H_2O, 0.1584. Calcd. for $C_{21}H_{32}O_2$: C, 79.69; H, 10.20. Found: C, 79.33; H, 10.28. Mol. wt. (cryoscopic in benzene). Subs., 0.1513; benzene, 13.1765; Δ^t, 0.195°. Calcd. for $C_{21}H_{32}O_2$: mol. wt. 316.4. Found: 301.5.

Cyclohexyl-di-*tert.*-butylethinylbromomethane.—Five grams of the carbinol was dissolved in 25 cc. of petroleum ether (b. p. 20–40°) and treated with 2 g. of phosphorus tribromide as described under *tert.*-butyl-di-*tert.*-butylethinylbromomethane. The crude bromide was isolated and used in subsequent experiments without purification as it was feared that distillation would cause the elimination of hydrogen bromide from the molecule.

Cyclohexyl-di-*tert.*-butylethinylchloromethane.—Five grams of the carbinol was dissolved in 15 cc. of dry benzene and 1.8 g. (10% excess) of acetyl chloride was added. The mixture was allowed to stand for twenty-four hours with occasional shaking. The benzene was then evaporated under reduced pressure and 5 cc. of absolute methyl alcohol was added to destroy the excess acetyl chloride. The methyl acetate was then evaporated under reduced pressure. The crude chloride was used for subsequent experiments.

Cyclohexyl-di-*tert.*-butylethinylmethyl Methyl Ether.—Ten grams of carbinol was dissolved in 10 cc. of absolute methyl alcohol (5 times the theoretical amount) and 0.4 cc. of concentrated sulfuric acid (sp. gr. 1.84) was slowly added with shaking and cooling. The amount of acid added did not exceed 3% of the total weight. The mixture separated into two layers within a few hours. The reaction was complete in twenty-four hours. Water was then added and the organic material was extracted with ether. The ether layer was dried over magnesium sulfate and the solvent evaporated. The residue was distilled under diminished pressure and the fraction boiling at 116–121° at 3.5 mm. was collected. The yield was 5 g. (52.6% of the theoretical amount). The constants found were: sp. gr. $^{20}_{20}$, 0.8680; n^{20}_{D} 1.4640. Calcd. for $C_{28}H_{32}O$: M_{D}, 90.04. Found: M_{D}, 91.55.

Anal. Subs., 0.1865: CO_2, 0.5683; H_2O, 0.1887. Calcd. for $C_{20}H_{32}O$: C, 83.33; H, 11.11. Found: C, 83.10; H, 11.32.

***Sym.*-di-cyclohexyl-tetra-*tert.*-butylethinylethane.** **(A)** From the Bromide and Molecular Silver.—The crude bromide from 2 g. of carbinol was dissolved in 10 cc. of dry ether and was shaken mechanically for twenty-four hours with 2 g. of molecular silver in an atmosphere of dry nitrogen. The ether solution was then filtered, concentrated to about 2 cc. under reduced pressure and 5 cc. of absolute alcohol was added. The concentration was continued until crystals appeared and the mixture was then cooled. The solid material was filtered and recrystallized from an ether–alcohol mixture. It melted at 149–150°.

(B) From the Bromide and Liquid Sodium–Potassium Alloy.—The alcoholic filtrate from the above hydrocarbon was evaporated to dryness under diminished pressure. The residue contained bromine. It was dissolved in 10 cc. of dry ether and shaken for twenty-four hours with 3 4 cc. of sodium–potassium alloy in an atmosphere of dry nitrogen. The solution had a reddish-brown tint. It was treated with dry carbon dioxide and worked up as described under *tert.*-butyl-di-*tert.*-butylethinylacetic acid. The ether contained more of the hydrocarbon obtained above, m. p. 149–150°. A small amount of acid was isolated as a yellow powder (m. p. 114–117°). Further treatment of this will be described later. Several runs of the bromide were then treated directly with liquid sodium–potassium alloy. The results were exactly the same.

(C) From the Bromide and 40% Sodium Amalgam.—The bromide from 5 g. of carbinol was dissolved in 50 cc. of dry ether and placed in a 250-cc. flask. Forty grams of 40% sodium amalgam was added, the flask was filled with nitrogen and the mixture was shaken mechanically for twenty-four hours. The amalgam was frozen and the ether decanted into a 3-liter nitrogen-filled flask. The amalgam was washed once with 50 cc. of petroleum ether (b. p. 40–60°), freshly dried over ethylmagnesium bromide. The petroleum ether washing was also poured into the 3-liter flask and 100 cc. of dry petroleum ether was added to insure precipitation of all metal alkyl. A cloth filter reinforced by copper gauze was then fitted to the flask which was inverted and the petroleum ether filtered out while maintaining a nitrogen atmosphere.

The petroleum ether was evaporated to dryness under reduced pressure and the residue was recrystallized from ether–alcohol mixture. Three-fourths of a gram of the same hydrocarbon described above was obtained, m. p. 149–150°. There was no depression of the melting point when it was mixed with the hydrocarbon from the reaction of silver with the bromide.

Anal. Subs., 0.1404, 0.1815: CO_2, 0.4542, 0.5898; H_2O, 0.1436, 0.1753. Calcd. for $C_{38}H_{58}$: C, 88.82; H, 11.38. Found: C, 88.42, 88.62; H, 11.45, 10.81. *Mol. wt.*

(cryoscopic in benzene). Subs., 0.3138; benzene, 13.1765; Δ^t, 0.253°. Calcd. for $C_{38}H_{58}$: mol. wt., 514. Found: 482.

About 100 cc. of diethyl ether, freshly dried over ethylmagnesium bromide, was added to the residue of metal alkyl in the 3-liter flask. To this was added 0.5 g. of tetramethylethylene dibromide dissolved in 25 cc. of dry ether. The ether solution was then filtered and concentrated to dryness under reduced pressure. The residue was kept under reduced pressure for some time in order to volatilize the excess tetramethylethylene dibromide. It was then recrystallized from an ether–alcohol mixture. The yield was 0.1 g. of the same hydrocarbon. Apparently very little metal alkyl had formed in the reaction.

(D) From the Chloride and 40% Sodium Amalgam.—The chloride prepared from 5 g. of carbinol as previously described was treated with 40 g. of 40% sodium amalgam for a twenty-four hour period. Dry carbon dioxide was then passed into the reaction mixture. The amalgam was frozen and the ethereal suspension of the acid salt was decanted. This was worked up as described under *tert.*-butyl-di-*tert.*-butylethinylacetic acid. About 0.2–0.3 g. of a yellow powder was isolated which melted between 114–117° as did the acid from the reaction of sodium–potassium alloy on the bromide.

From the ether solution a small amount of hydrocarbon, m. p. 146–148°, was isolated with difficulty as it tended to form a paste.

(E) From the Methyl Ether of the Carbinol.—Three and one-half grams of cyclohexyl-di-*tert.*-butylethinylmethyl methyl ether was dissolved in 50 cc. of dry ether, placed in a nitrogen filled flask, and 10 cc. of liquid, sodium–potassium alloy was added. This was shaken for twenty-four hours. The reaction mixture became yellowish-brown in color. Then 2 g. of powdered potassium was introduced into the flask and shaking was continued for another twenty-four hours. The ether suspension was then decanted from the excess alloy into another nitrogen-filled flask fitted with a dropping funnel. From the dropping funnel was added 1.4–1.8 g. of tetramethylethylene dibromide dissolved in 25 cc. of dry ether. The yellowish brown tint of the reaction mixture slowly changed to light greenish blue. A small amount of alcohol was added to decompose any particles of the alloy, and then the ether solution was washed with water. The ether layer was dried over magnesium sulfate and the ether evaporated under reduced pressure. The residue was kept under diminished pressure for some time to remove all traces of tetramethylethylene dibromide. It was then recrystallized from an ether–alcohol mixture and melted at 149–150°. The yield of hydrocarbon was 0.8 g. (27% of the theoretical amount).

The hydrocarbon isolated in all five of the reactions as just described was undoubtedly the desired *sym.*-dicyclohexyl tetra-*tert.*-butylethinylethane.

Cyclohexyl-di-*tert.*-butylethinylacetic Acid. (A) From the Bromide and Chloride.—The isolation of an acid from the action of sodium–potassium alloy on the bromide, and also from the action of 40% sodium amalgam on the chloride, has already been mentioned. The acids from both sources melted in a similar fashion so they were combined and recrystallized from glacial acetic acid. The product was then pure white and melted at 125–126°.

Neutral equivalent. Subs., 0.1170: 3.30 cc. of 0.1163 N NaOH. Calcd. for $C_{20}H_{30}O_2$: 302. Found: 304.6.

(B) From the Methyl Ether of the Carbinol.—One and eight-tenths grams of the methyl ether of cyclohexyl-di-*tert.*-butyl-ethinylcarbinol was dissolved in 15 cc. of dry ether and shaken with 4–5 cc. of sodium–potassium alloy in an atmosphere of dry nitrogen for twenty-four hours. Dry carbon dioxide was then passed into the reaction mixture and the red color of the metal alkyl disappeared immediately. The ethereal suspension of the sodium salt of the acid was decanted from the excess alloy and water was added cautiously to the ether. The ether layer was extracted several times with water. The aqueous extracts were combined, cooled to 5° and acidified with dilute hydrochloric acid. The organic acid separated in white flocculent crystals, which were filtered. It was recrystallized from glacial acetic acid and melted at 125–126°. The yield was 0.5 g. (27% of the theoretical amount). When a sample of this acid was mixed with that obtained from the bromide and chloride, there was no depression of the melting point.

Anal. Subs., 0.1757: CO_2, 0.5090; H_2O, 0.1589. Calcd. for $C_{20}H_{30}O_2$: C, 79.41; H, 10.00. Found: C, 78.87; H, 10.10.

Di-*tert.*-butylethinyl-cyclohexylidenemethane.—Twenty-eight grams of cyclohexyl-di-*tert.*-butylethinylcarbinol was heated to 125–130° for twelve hours with 28 g. of potassium acid sulfate. The water was removed as formed by means of a current of dry air. The reaction mixture was extracted with ether and dried over magnesium sulfate. The solvent was evaporated and the residue distilled under diminished pressure. The portion boiling at 105–110° at 3 mm. was collected. The yield was only 5 g. The product gave an intense coloration when treated with tetranitromethane, whereas the carbinol gave no coloration with that reagent; sp. gr. $^{20}_{20}$, 0.8578; $n^{20}_{\rm D}$ 1.4838.

Anal. Subs., 0.1676: CO_2, 0.5485; H_2O, 0.1635. Calcd. for $C_{19}H_{28}$: C, 89.06; H, 10.94. Found: C, 89.25; H, 10.92.

Chlorocyclohexyl-di-*tert.*-butylethinylmethane.—Five grams of di-*tert.*-butylethinyl-cyclohexylidenemethane was dissolved in 25 cc. of absolute alcohol. Dry hydrogen chloride was passed into the ice-cooled solution until it was saturated. The solution was then warmed to 40° for one-half hour and again saturated with dry hydrogen chloride. The alcohol was removed under reduced pressure. The residue was dissolved in dry ether and anhydrous sodium carbonate was added. The ether was evaporated under reduced pressure. There was left a brown oil which contained chlorine.

Anal. (Stepanow). Subs., 0.2263: 7.91 cc. of 0.1005 N $AgNO_3$. Calcd. for $C_{19}H_{29}Cl$: Cl, 12.14. Found: Cl, 12.43.

This oil was dissolved in 50 cc. of dry ether and shaken with 30 g. of 40% sodium amalgam for twenty-four hours in an atmosphere of dry nitrogen. Dry carbon dioxide was passed into the reaction mixture and it was worked up as described in the preparation of dicyclohexyl-tetra-*tert.*-butylethinylethane from the bromide and 40% sodium amalgam. No acid was isolated. From the ether there was isolated a light yellow oil, b. p. 105–110° at 3 mm.; $n^{20}_{\rm D}$ 1.4843. This oil gave an intense coloration with tetranitromethane. It was di-*tert.*-butylethinyl-cyclohexylidenemethane.

Summary

1. *Sym.*-di-*tert.*-butyl-tetra-*tert.*-butylethinylethane has been prepared by the action of silver on *tert.*-butyl-di-*tert.*-butylethinylbromomethane.

2. This hydrocarbon reacted with liquid sodium–potassium alloy to form the alkali metal derivative of *tert.*-butyl-di-*tert.*-butylethinylmethyl. It did not react with 40% sodium amalgam. It was not affected by heat and was more stable than *sym.*-di-phenyl-tetra-*tert.*-butylethinylethane.

3. *Sym.*-dicyclohexyl-tetra-*tert.*-butylethinylethane has been prepared by several methods. This hydrocarbon was not cleaved by liquid sodium–potassium alloy.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF QUEEN'S UNIVERSITY AND BISHOP'S UNIVERSITY]

THE CONDENSATION OF BENZOIN AND BENZIL WITH ETHYL CYANO-ACETATE[1]

BY JOHN A. MCRAE AND ALBERT L. KUEHNER

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Numerous interesting condensations of various types of ketones and aldehydes, capable of being expressed in enolic forms, with ethyl cyano-acetate, have been described by several authors,[2] most of whom interpreted their results on the basis that the ketone or aldehyde first reacts in its enolic form with the sodio derivative of ethyl cyano-acetate, eliminating water and giving β,γ-unsaturated cyano esters or acids. This mode of interpretation was shown by Lapworth and McRae[3] to have led to an erroneous conclusion in the condensation of cyclohexanone with ethyl cyano-acetate and Kohler and Corson[4] have demonstrated that it is clearly inapplicable in certain cases. Ingold,[2d] who has used this mechanism most recently, has now[5] abandoned it in favor of the mechanism emphasized by Lapworth and McRae, which leads to an α,β-unsaturated structure for the substances produced initially (if the aldol stage be omitted), although subsequent isomeric changes may yield a β,γ-unsaturated form. In view of the uncertainty which, therefore, is attached to the structures previously assigned to many of the substances described in the foregoing papers[2] it has seemed to us desirable to reinvestigate some of the more interesting cases in which it appears that the initial condensation has been followed by further reactions.

In the present communication we describe the results obtained on investigating the condensation of benzoin with ethyl cyano-acetate[2b] and the related condensation of benzil and ethyl cyano-acetate. We have also compared the behavior toward hydrogen cyanide of the product from the latter condensation with that of ethyl camphorylidene-cyano-acetate, derived from condensing camphorquinone (a 1,2-diketone) with ethyl cyano-acetate.[6]

Haworth obtained an acid, $C_{20}H_{14}O_4N_2$, m. p. 136°, by condensing

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[1] We gratefully acknowledge our indebtedness to the Canadian National Research Council for the award of a bursary in 1924–1925 to one of us (A. L. K.), during the tenure of which most of the work here described was carried out.

[2] (a) Harding, Haworth and Perkin, J. *Chem. Soc.*, 93, 1943 (1908); (b) Haworth, *ibid.*, 95, 480 (1909); (c) Gardner and Haworth, *ibid.*, 95, 1955 (1909); Harding and Haworth, *ibid.*, 97,486 (1910); Simonsen and Nayak, *ibid.*, 107, 792 (1915); (d) Ingold and Thorpe, *ibid.*, 115,143 (1919).

[3] Lapworth and McRae, *ibid.*, 121,2741 (1922).

[4] Kohler and Corson, THIS JOURNAL, 45,1975 (1923).

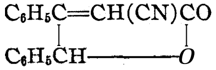
[5] Ingold, J. *Chem. Soc.*, 184 (1930).

[6] Forster and Withers, *ibid.*, 101, 1327 (1912).

benzoin with ethyl cyano-acetate in the presence of sodium ethoxide and assigned to it the structure α,δ-dicyano-β,γ-diphenyl-Δ^{β}-butene-α,δ-dicarboxylic acid (I), based solely on the assumption that benzoin had

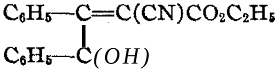
$$COOHCH(CN)C(C_6H_5){=}C(C_6H_5)(CN)COOH \quad I$$

reacted in its enolic form $C_6H_5C(OH){=}C(OH)C_6H_5$. We have carried out this condensation many times and have followed scrupulously Haworth's directions but we have failed to isolate a substance agreeing in properties or analysis with that described by Haworth. On the contrary, we have obtained consistently by acidification of the reaction mixture a substance, m. p. 141°, having the formula $C_{17}H_{11}O_2N$. The substance dissolves slowly in caustic soda and has an equivalent of **264** ($C_{17}H_{11}O_2N$ requires **261**). Evidently it has been formed by the condensation of equimolecular proportions of the reactants and the only satisfactory structure we are able to assign to it is that of the *lactone **of** α-cyano-β,γ-diphenyl-γ-hydroxycrotonic **acid*** (II). This lactone has been formed apparently by the hydrolysis of the ester (111), followed by elimination of water.



$$\begin{array}{l} C_6H_5C{=}CH(CN)CO \\ \quad | \qquad\qquad\quad | \\ C_6H_5CH\text{————}O \end{array}$$

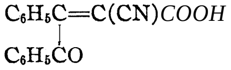
II



$$\begin{array}{l} C_6H_5\text{—}C{=}C(CN)CO_2C_2H_5 \\ \qquad\ | \\ C_6H_5\text{—}C(OH) \end{array}$$

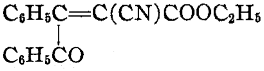
III

In agreement with the structure assigned, the substance is oxidized to benzil by chromic acid and to *α-cyano-β-benzoylcinnamic **acid*** (IV), by dilute nitric acid. The latter is identical with the acid produced by hydrolyzing ethyl *α-cyano-β-benzoylcinnamate* (V), which was obtained by condensing benzil with ethyl cyano-acetate.



$$\begin{array}{l} C_6H_5C{=}C(CN)COOH \\ \quad\ | \\ C_6H_5CO \end{array}$$

IV

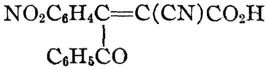


$$\begin{array}{l} C_6H_5C{=}C(CN)COOC_2H_5 \\ \quad\ | \\ C_6H_5CO \end{array}$$

V

An attempt was made to prepare ethyl α-cyano-β,γ-diphenyl-γ-hydroxycrotonate (III), by acting on the supposed silver salt of the corresponding acid formed from the lactone with ethyl iodide, but ethyl benzoyl α-cyanocinnamate was obtained instead, the corresponding silver salt having evidently been produced on dissolving the lactone in ammonia and treating the neutral solution with silver nitrate, oxidation taking place during the process.

The action of concentrated nitric acid on the lactone gave a markedly acidic substance, *α-cyano-β-benzoyl-β-(m-nitrophenyl)-acrylic **acid*** (VI).



$$\begin{array}{l} NO_2C_6H_4C{=}C(CN)CO_2H \\ \qquad\quad\ | \\ \qquad C_6H_5CO \end{array}$$

VI

This on oxidation gave an excellent yield of m-nitrobenzil (m. p. 118") which Chattaway and Coulson[7] recently described, having isolated it

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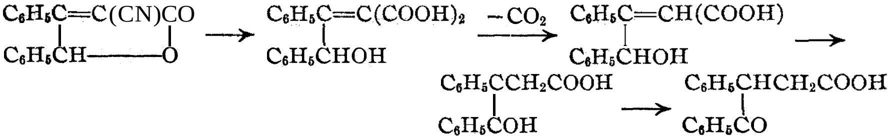
[7] **Chattaway and** Coulson, *J. Chem. Soc.*, 1080 (1928).

(m. p. 120°) in small quantity from the action of nitric acid on benzoin. On account of the markedly different yields in the two processes by which m-nitrobenzil is obtained, we assign the nitro group in (VI) to the benzene radical in closest proximity to the $=C(CN)COOH$ group, although no other case of this group acting as a meta directing group has been observed. The identification of our substance as m-nitrobenzil followed from its oxidation by chromic acid into benzoic and m-nitrobenzoic acids, both of which were fully identified.

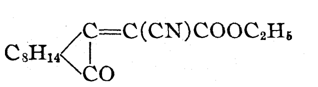
The foregoing lactonic structure is also in agreement with the behavior of the substance toward concentrated sulfuric acid, which converts it into β-phenyl-β-benzoylpropionic acid, whose identity was proved by direct comparison with a specimen prepared according to the description of Avery and McDole.[8] This conversion arises as follows



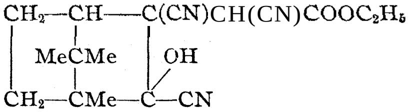
$$\begin{array}{l} C_6H_5C{=}C(CN)CO \\ \quad | \qquad\qquad | \\ C_6H_5CH{-\!-\!-}O \end{array} \longrightarrow \begin{array}{l} C_6H_5C{=}C(COOH)_2 \\ \quad | \\ C_6H_5CHOH \end{array} \xrightarrow{-CO_2} \begin{array}{l} C_6H_5C{=}CH(COOH) \\ \quad | \\ C_6H_5CHOH \end{array} \longrightarrow \begin{array}{l} C_6H_5CCH_2COOH \\ \quad | \\ C_6H_5COH \end{array} \longrightarrow \begin{array}{l} C_6H_5CHCH_2COOH \\ \quad | \\ C_6H_5CO \end{array}$$

Forster and Withers[6] state that benzil had been condensed with ethyl cyano-acetate in Dr. Forster's laboratory but a description of the substance obtained was not published. The condensation, we have found, takes place readily with the formation of ethyl *α-cyano-β-benzoylcinnamate* (V), which curiously has the same melting point as the lactone (II) but analyses, a mixed melting point determination and hydrolysis of (V) to the acid (IV) all show that the two substances are not identical. With neither the lactone (II) nor the ester (V) were we able to effect the addition of hydrogen cyanide, a reaction which is characteristic of simple cyano-acrylic acids and esters.[9] The condensation of benzil with ethyl cyano-acetate adds another example of the occurrence of condensation between ethyl cyano-acetate and a ketone in which there is no possibility of enolization. However, we were unable to bring about condensation between ethyl cyano-acetate and the methyl ether of benzoin.

In contrast with the behavior of the ester (IV) toward hydrogen cyanide, ethyl camphorylidene-cyano-acetate (VII) reacts rapidly and adds on



VII



VIII

hydrogen cyanide both at the ethenoid linkage and the carbonyl linkage as well, giving *ethyl 1,7,7-trimethyl-2,3-dicyano-2-hydroxy-bicyclo-(1,2,2)-heptane-3-cyano-acetate* (VIII). This addition reaction agrees with the

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[8] Avery and McDole, THIS JOURNAL, 30, **1423** (1908).

[9] *Cf.* Lapworth and McRae, Ref. 3.

structure given their substance by Forster and Withers, who rejected the alternative β,γ-unsaturated formula. This ester loses hydrogen cyanide readily on treatment with alcoholic potash, giving presumably (α'-cyano-camphoryl)-α-cyano-acetic acid (IX),  $C_8H_{14}\left\langle\begin{array}{l}C(CN)CH(CN)COOH\\ |\\ CO\end{array}\right.$ (m. p. 107–109°), although the substance has not been complĕtely identified.

Experimental

Lactone of α-Cyano-β,γ-diphenyl-γ-hydroxycrotonic Acid. (II).—To a mixture of 21.2 g. of benzoin in 70 cc. of absolute alcohol there was added 14 g. of ethyl cyanoacetate followed by 2.3 g. of sodium dissolved in 70 cc. of absolute alcohol. There is a momentary purple color on adding sodium and heat is developed. On shaking the benzoin dissolved to form a clear reddish solution. This was heated on the water-bath under a reflux condenser for three hours, after which it was poured into 800 cc. of water. A small precipitate of unchanged benzoin was filtered off and the clear filtrate acidified. A granular semi-solid precipitate was filtered off, rubbed with a small amount of ether and the white crystals filtered from the ether; yield about 85%. Recrystallization from alcohol yielded white needles melting at 141°, soluble in chloroform, benzene and alcohol, nearly insoluble in ether.

Anal. Calcd. for $C_{17}H_{11}O_2N$: C, 78.1; H, 4.22; N, 5.36; equivalent, 261. Found: C, 77.5; H, 4.26; N, 5.48; equivalent, 264.

The lactone absorbs bromine only very slowly and failed to add hydrogen cyanide.

Hydrolysis of the **Lactone α-Cyano-β,γ-diphenyl-γ-hydroxycrotonic** Acid to **β-Phenyl-β-benzoylpropionic** Acid.—The lactone (5.2 g.) was heated with 85 cc. of concentrated sulfuric acid and 50 cc. of water at a temperature of 130–140° for five hours. The mixture after standing overnight was poured on 400 g. of cracked ice and the precipitated semi-solid brown mass was filtered off. This was warmed with a solution of dilute caustic soda and a small amount of insoluble material filtered out. The alkaline solution was acidified, when a mass of brown crystals was obtained (2.3 g.). Three recrystallizations from alcohol failed to remove a brown color. After boiling with charcoal colorless octahedra were obtained, m. p. 160.5".

This substance was found to be identical with β-phenyl-β-benzoylpropionic acid made by oxidizing β,γ-diphenyl-γ-cyanobutyric acid according to the method of Avery and McDole[8] no depression of the melting point being observed on making a mixed melting point determination.

α-Cyano-β-(m-nitrophenyl)-β-benzoylacrylic Acid.—The lactone (40 *g.)* was heated under a reflux with concd. nitric acid (200 cc.) until the evolution of brown fumes ceased (about one hour). On cooling, pure white crystals separated which were filtered and washed thoroughly with water. It is necessary to allow the crystals to separate here, for, if the clear solution is poured into water, a sticky semi-solid mass is obtained from which pure crystals are obtained with some difficulty. After twice recrystallizing from alcohol, the substance softens at 212" and melts at 218–220° with decomposition; yield of pure crystals, 41%.

Anal. Calcd. for $C_{17}H_{10}O_5N_2$: C, 63.3; H, 3.11; N, 8.7; equivalent, 322. Found: C, 63.1; H, 3.18; N, 9.14; equivalent, 323.

The substance is soluble in hot chloroform, alcohol and benzene but insoluble in ligroin. From alcohol the crystals are obtained as colorless needles.

α-Cyano-β-(m-nitrophenyl)-β-benzoylacrylic acid can also be obtained by oxidizing ethyl α-Cyano-β-benzoylcinnamate with concentrated nitric acid.

Oxidation of α-Cyano-β(-*m*-nitrophenyl)-β-benzoylacrylic Acid to *m*-**Nitrobenzil.**—The acid (10 g.) was dissolved in 80 cc. of acetone and a saturated aqueous solution of potassium permanganate slowly added until an excess was present. The reaction mixture was kept cool during the addition of the permanganate. The mixture was allowed to stand for one hour and then the heavy precipitate of manganese dioxide was cleared by passing in sulfur dioxide and adding sulfuric acid. The yellow precipitate of nitrobenzil was filtered and recrystallized from alcohol as pale yellow crystals, m. p. 117–118°; yield, 60–70%.

This substance was shown to be *m*-nitrobenzil by oxidizing with chromic acid in boiling acetic acid solution. The mixture of m-nitrobenzoic acid and benzoic acid was separated by forming the methyl ester and recrystallizing from alcohol.

Anal. Calcd. for $C_{14}H_9O_4N$: N, 5.49. Found: N, 5.82.

α-Cyano-β-benzoylcinnamic Acid. Oxidation of **Lactone** of α-**Cyano**-β,γ-**diphenyl**-γ-**hydroxycrotonic** Acid to α-Cyano-β-benzoylcinnamic Acid.—Six g. of the lactone was boiled gently under a reflux condenser with 48 cc. of concentrated nitric acid to which had been added 12 cc. of water. When the evolution of brown fumes had ceased, a small amount of water was added and the solution cooled. A yellow semi-solid mass separated which was recrystallized twice from benzene and ligroin. The crystals soften at 112° and melt at 116–117°; yield, 5.4 g.

Anal. Calcd. for $C_{17}H_{11}O_3N\cdot{}^1/_2C_6H_6$: C, 75.9; H, 4.43; N, 4.43; equivalent, 316. Found: C, 75.5; H, 4.54; N, 5.03; equivalent, 317.

The crystals are soluble in alcohol, chloroform and hot benzene. The same substance can be obtained by oxidizing the lactone in hot acetic acid solution with concentrated nitric acid. These crystals were found to be identical with those prepared by the hydrolysis of ethyl α-cyano-β-benzoylcinnamate and also contained benzene of crystallization.

Attempted Esterification of the **Lactone** of α-Cyano-β,γ-diphenyl-γ-hydroxycrotonic Acid.—The lactone (5 g.) was dissolved in dilute ammonia and the excess ammonia boiled off. The solution was cooled and silver nitrate was added. A white precipitate was formed which immediately turned black. This silver salt was dried over sulfuric acid and boiled with 15 g. of ethyl iodide in 40 cc. of dry ether for thirteen hours. The ethereal solution was filtered and evaporated, leaving a red oil which deposited a small amount of white crystals. After two recrystallizations these melted at 141° and were shown to be identical with the ethyl α-cyano-β-benzoylcinnamate obtained by condensing benzil with cyano-acetic ester.

Anal. Calcd. for $C_{19}H_{15}O_3N$: C, 74.7; N, 4.96. Found: C, 75.2; H, 5.18.

Preparation of Ethyl α-Cyano-β-benzoylcinnamate.—Benzil (8.4 g.) was added to a solution of 1 cc. of piperidine in 60 cc. of absolute alcohol. To this was added 9.02 g. of cyano-acetic ester, when a purple color was formed which disappeared almost immediately. The mixture was heated on a water-bath under a reflux condenser for five hours and allowed to stand overnight, when crystallization took place. After acidification the crystals were filtered and washed with alcohol and usually were found now to contain no unchanged benzil and gave a constant melting point of 141" without further purification; yield, 8.2 g.

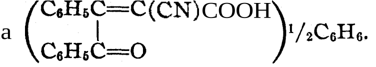
Anal. Calcd. for $C_{19}H_{15}O_3N$: C, 74.7; H, 4.96; N, 4.6. Found: C, 74.4; H, 4.97; N, 5.1.

It is necessary that alcohol be not used in excess of the amount mentioned to prevent the decomposition of the benzil into benzaldehyde and ethyl benzoate. Sodium ethylate may also be used as a condensing agent.

The ester crystallizes from alcohol as colorless needles and is soluble in benzene, chloroform and hot acetic acid. It does not absorb bromine.

Benzil is readily obtained from this ester by dissolving in acetone and adding an aqueous solution of potassium permanganate.

α-Cyano-β-benzoylcinnamic Acid.—Five grams of the ester was allowed to stand with a solution of potassium hydroxide in alcohol. After fifteen minutes the crystals had all dissolved and the solution no longer became turbid on diluting with water. This was poured into 300 cc. of water and acidified and the brown oil thrown down was extracted with ether. The ether was dried and evaporated and the brown oil dissolved in benzene. When ligroin was added an oil was again obtained which solidified on standing. After another recrystallization from benzene and ligroin white crystals were obtained which softened at 112° and melted at 116–117°; yield of pure crystals, 58%.

The substance was found to contain benzene of crystallization and have the constitution represented by the formula  $\left(\begin{array}{l} C_6H_5C{=}C(CN)COOH \\ \quad\ | \\ C_6H_5C{=}O \end{array}\right)\frac{1}{2}C_6H_6$. This substance gave an equivalent by titration of 318. Calcd. for $C_{17}H_{11}O_3N\cdot\frac{1}{2}C_6H_6$: equivalent, 316.

The benzene can be driven off by heating in an oven at 90° for several hours. The substance then melted at 135–136°; equivalent, 283. Calcd. for $C_{17}H_{11}O_3N$: equivalent, 277.

Colorless needle-like crystals, m. p. 135–136°, can be obtained by recrystallizing from alcohol.

Benzil can readily be obtained from α-cyano-β-benzoylcinnamic acid by oxidizing with potassium permanganate in sodium carbonate solution.

Ethyl (1,1,7)-Trimethyl-2,3-dicyano-2-hydroxy-bicyclo-(1,2,2)-heptane-3-cyano-acetate.—Ethyl camphorylidene-cyano-acetate (13.9 g.) prepared according to Forster and Withers[6] was dissolved in 85 cc. of absolute alcohol at 40–50°. Thirteen and seven-tenths g. of potassium cyanide in 40 *cc.* of water was added and the mixture kept at 40–50° for one hour. Six grams of glacial acetic acid in 25 cc. of water was added carefully without mixing. Overnight the product separated as long white needles. The solution had lost all of the yellow color of the camphorylidene-cyano-acetic ester, indicating that the reaction had gone to completion. The crystals were filtered and washed with 50% alcohol. The total yield obtained was almost the theoretical. After recrystallization from hot alcohol the crystals melted at 202–204°. The substance is soluble in hot alcohol, chloroform and benzene; $[\alpha]_D$ +115.1°.

Anal. Calcd. for $C_{17}H_{21}O_3N_3$: C, 64.8; H, 6.7; N, 13.3. Found: C, 64.6; H, 6.86; N, 13.3.

Summary

1. The lactone of α-cyano-β,γ-diphenyl-γ-hydroxycrotonic acid has been obtained as the principal product from the condensation of benzoin with ethyl cyano-acetate. Various reactions of this substance support the structure assigned.

2. m-Nitrobenzil is readily obtained by oxidizing the acid produced by nitrating the foregoing lactone.

3. Benzil has been condensed with ethyl cyano-acetate and the behavior of the product toward hydrogen cyanide has been compared with that of ethyl camphorylidene-cyano-acetate toward the same reagent.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

METALLIC SALTS OF KETONES

BY HAROLD H. STRAIN

RECEIVED MAY 19, 1930 PUBLISHED AUGUST 5, 1930

Upon attempting to use metallic amides as dehydrating agents to promote the reaction between ketones and liquid ammonia, the writer found that metallic salts of the ketones were formed.[1] A search of the literature then revealed that such salts had been prepared by the action of ketones on metallic amides in the presence of indifferent solvents,[2] and by the action of sodium on the ketones.[3]

Because of the very weak acid properties of the ketones, the use of the indifferent solvents as a liquid medium in the preparation of their salts has been requisite. In general such liquids are poor solvents for metallic salts, so that much difficulty is entailed in preparing and recrystallizing the latter. The poor ionizing properties of the common indifferent solvents also causes the reaction between the ketone and the metallic amide to proceed very slowly.

Since liquid ammonia possesses unique ionizing, solvolyzing and solvent properties which make it an advantageous medium for preparing salts of very weak acids,[4] it was tested as a solvent for the salts of ketones and found to serve admirably. The salts prepared by its use are described below.

Methods

All salts were prepared and purified in liquid ammonia solution. The methods of handling the ammonia were essentially the same as those described by Franklin.[5]

The salts were formed in two-legged tubes by pouring a solution of the ketone over an excess of the metallic amide. After the reaction had run to completion the solution was decanted from excess amide and concentrated until crystals separated. The crystals were then washed with liquid ammonia and dried in vacuum. The tube was subsequently opened by scratching with a file and breaking with a drop of hot glass. The end of the tube containing the crystals was stoppered and the weight of the sample deter-

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[1] Strain, THIS JOURNAL, 52, 820 (1930).

[2] Merling, Chrzesciuski and Pfeffer, U. S. Patent 1,169,341, January, 1925; *C. A.*, 10, 952 (1916).

[3] Haller, "Dissertation," Nancy, 1879, p. 41. Haller and Bauer [Ann. *chim. phys.*, [8] 28, 373 (1913); [8] 29, 313 (1913)] have shown that many ketones are alkylated when treated with sodium amide and an alkyl halide, a reaction which indicates the intermediate formation of a salt of the ketone.

[4] Franklin, *J. Phys. Chem.*, 24, 81 (1920); Strain, THIS JOURNAL, 49, 1995 (1927); Cornell, *ibid.*, 50, 3311 (1928).

[5] Franklin, *J. Phys. Chem.*, 15, 513 (1911); Ref. 4.

mined by weighing the stoppered tube before and after removing a portion of the salt to a platinum crucible. Sodium and potassium were determined as sulfates, calcium as the oxide.

All salts are stable to 60° either in *vacuum* or in an atmosphere of ammonia. Exposed to the air, however, they undergo a very vigorous decomposition. They are rapidly hydrolyzed by water to the ketone and the metallic hydroxide.

TABLE I

SALTS OF KETONES

Ketone	Metal	Formula	Cryst. form	Color	Soly.	Metal, % Calcd.	Metal, % Found
Acetone[a]	Na	C_3H_5ONa	......	None	Very	28.8	29.2
	Ca	$(C_3H_5O)_2Ca$	......	None	Very	26.0	26.3
Methylpropyl	Na	C_5H_9ONa	None	None	Very	21.3	24.5
Acetophenone	Na	C_8H_7ONa	......	None	Very	16.2	16.9
	Ca	$(C_8H_7O)_2Ca$	Prisms	None	Sol.	14.4	14.2
Methyl *p*-tolyl	Na	C_9H_9ONa	None	...	Very	14.8	15.4
Camphor	Na	$C_{10}H_{15}ONa$	....	None	Med.	13.2	13.8
Fenchone	Na	$C_{10}H_{15}ONa.XNH_3$	Distorted cubes	None	Sl.	..	..
		$C_{10}H_{15}ONa$	Amorphous	White	...	13.2	12 6
Benzophenone[b]	Na	$C_{13}H_{10}ONaNH_2$	Short needles	None	Sol.	10.4	11.0
	K	$C_{13}H_{10}ONK_3$	Flakes	None	Sl.	37.4	39.8 40.8
				Nitrogen, calcd.		4.5	6.0

[a] For references relating to the preparation of metallic salts of acetone in indifferent solvents see Bacon and Freer, C. A., 1, **1695 (1906);** Bayer and Company, *ibid.*, 10, **2615 (1916).**

[b] Haller and Bauer [*Ann. chim. phys.*, [8] 16, **146 (1909)**] report the formation of a compound having the formula $(C_6H_5)_2C(NH_2)ONa$ which they analyzed and found to contain **10.6–10.9%** sodium. These values are in rather good agreement with the theoretical value, which is 10.4%, rather than **11.7%** as given by Haller and Bauer. The potassium salt of benzophenone represents a rather unusual compound. For a time it appeared that this salt might be dipotassium benzamide, which should contain 39.7% potassium [Pauline Lucas, *ibid.*, [8] 17, **127** (1909)]. However, benzamide does not form a dipotassium salt [Ruth Fulton, "Thesis," Stanford University (1926)]. This salt is also quite different from the dipotassium derivative of benzophenone prepared by the action of potassium on benzophenone [Wooster, THIS JOURNAL, 50, **1388 (1928);** *ibid.*, **51,1856** (1929)].

Summary

A number of metallic salts of ketones have been prepared by the action of metallic amides on ketones in liquid ammonia.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND ENTOMOLOGY, IOWA STATE COLLEGE]

CATALYTIC REDUCTION OF NICOTINE AND METARICOTINE

BY W. R. HARLAN[1] WITH R. M. HIXON

RECEIVED MAY 20, 1930 PUBLISHED AUGUST 5, 1930

In the study of the toxicity to insects of compounds structurally related to nicotine, considerable quantities of the reduced derivatives of nicotine were desired. The catalytic reduction of nicotine by means of platinum-oxide platinum black and hydrogen as used by Smith[2] on the dipyridyls and by Hamilton and Adams[3] on the pyridine and quinoline derivatives was selected as the most feasible method of preparation. During the course of these investigations, this method was also used by LaForge[4] for the reduction of metanicotine to dihydrometanicotine.

Nicotine was first reduced by Liebrecht[5] by the use of sodium in absolute alcohol. Since he regarded nicotine as hexahydrodipyridyl, he described the reduction product as β,β'-dipiperidyl. Pinner,[6] after establishing the constitution of nicotine, considered that the above reduction yielded largely hexahydronicotine. Blau[7] showed the majority of the reduction products to consist of octahydronicotine (also called octahydrometanicotine by Maass and Hildebrandt)[8] together with some hexahydronicotine. Both the method of reduction and the method of separation used in these studies would preclude their use as methods of preparation for any quantity of these derivatives.

Contrary to expectations, in the catalytic reduction of nicotine, rupture of the pyrrolidine ring takes place simultaneously with the hydrogenation of the pyridine ring. Complete reduction with the absorption of **3.7** moles of hydrogen to each mole of nicotine hydrochloride gives a mixture containing 25% hexahydronicotine hydrochloride and 75% octahydronicotine hydrochloride. If the reduction is interrupted at the point where three moles of hydrogen have been absorbed for each mole of nicotine hydrochloride (theoretical amount for reduction to hexahydronicotine), the resulting mixture consists of **19%** hexahydronicotine hydrochloride, **57%** octahydronicotine hydrochloride and 21% unchanged nicotine hydrochloride. An efficient method of separation for such a mixture has been

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[1] These studies were made possible by a fellowship maintained by the Tobacco By-Products and Chemical Corporation under the joint supervision of the Departments of Entomology and Chemistry at Iowa State College.

[2] Smith, THIS JOURNAL, 50, 1936 (1928).

[3] Hamilton and Adams, *ibid.*, 50, 2260 (1928).

[4] LaForge, *ibid.*, 50, 2483 (1928).

[5] Liebrecht, Ber., **18**, 2969 (1885).

[6] Pinner, *ibid.*, 26, 765 (1893).

[7] Blau, *ibid.*, 26, **628**, 1029 (1893).

[8] Maass and Hildebrandt, *ibid.*, **39**, 3700 (1906).

devised by taking advantage of the differences in solubilities of the hydrochlorides and picrates.

The catalytic reduction of metanicotine to dihydrometanicotine as carried out by LaForge[4] was duplicated. The complete reduction to octahydronicotine is also reported in the experimental data.

The compounds, with their constants and a suitable derivative, are listed in Table I. The hydrochlorides are hygroscopic and as a rule not suitable for characterization of the bases. The picrates of nicotine and dihydrometanicotine melt at 162 and 163°, respectively, so that this derivative cannot be used to distinguish between these compounds. The picrate of octahydronicotine is difficult to obtain sufficiently pure so that it will not be oily, while the bis-phenylsulfone derivative is easily prepared and melts sharply.

TABLE I

CONSTANTS AND REFERENCES TO COMPOUNDS SUITABLE POR CHARACTERIZATION OP THE REDUCED NICOTINE DERIVATIVES

		B. p. of free base, °C.	Suitable deriv.	M. p., °C.
Nicotine	$C_{10}H_{14}N_2$	246[a]	Picrate	218[b]
Metanicotine	$C_{10}H_{14}N_2$	276[c]	Chloroplatinate	255[c]
Dihydrometanicotine	$C_{10}H_{16}N_2$	259[d]	Chloroplatinate	199[d]
Hexahydronicotine	$C_{10}H_{20}N_2$	246[e]	Picrate	202"
Octahydronicotine	$C_{10}H_{22}N_2$	259[f]	Hydrochloride	202[f]
			Bis-phenylsulfone	143.5"

[a] Wolffenstein, "Pflanzenalkaloide," Julius Springer, Berlin, 1922, 3d ed., p. 136. [b] Pinner and Wolffenstein, Ber., **24,** 66 (1891). [c] Pinner, *ibid.*, **27,** 1053 (1894). [d] Löffler and Kober, *ibid.*, 42, 3431 (1909). [e] Blau, *ibid.*, 26, 1029 (1893). Hexahydronicotine is a solid melting at 36–37' when absolutely anhydrous. Blau gives the m. p. 198–201° for the picrate; when pure, the melting point is 202" sharp. [f] Blau, *ibid.*, 26, 628 (1893).

Experimental

Nicotine Hydrochloride.—The standard methods of obtaining pure nicotine depend upon fractional extraction between ether and water and final purification by distillation. A more convenient method has been found in the direct crystallization of the hydrochloride salt using a commercial product containing 95% water-free nicotine as a source When dry hydrogen chloride gas is passed into an ether solution of commercial 95% nicotine containing a small amount of acetone, crystallization of nicotine hydrochloride takes place with little difficulty. Sufficient hydrogen chloride gas should not be added to completely precipitate the nicotine as considerable amounts of the oily impurities present come down with the last portions of the nicotine hydrochloride. The small amount of acetone present in the ethereal solution serves to aid crystallization. After precipitation of the nicotine hydrochloride, it was rapidly filtered on a Buchner funnel and twice recrystallized from a mixture of absolute alcohol and acetone. This was accomplished by dissolving the hydrochloride in a small amount of hot absolute alcohol and adding acetone until the solution just became turbid. "Seeding" at this stage aided materially in crystallization. After cooling, the crystallized salt was rapidly filtered and the above procedure repeated. Because of the very deliquescent nature of nicotine hydrochloride, it was stored over calcium chloride or stick sodium hydroxide, the latter serving to remove any occluded hydrogen chloride present.

Metanicotine Hydrochloride.—Metanicotine was prepared according to Löffler's and Kober's[9] modification of Pinner's[10] method involving the formation and subsequent hydrolysis of benzoylnicotine. This method was also used by LaForge.[4]

The traces of unchanged nicotine can be removed from the benzoylnicotine by washing with dilute acetic acid, the weakly basic benzoyl derivative being only slightly soluble. The hydrochloride of the free base was prepared and recrystallized as described above for nicotine.

Catalyst and Reduction Apparatus.—The platinum-oxide platinum black was prepared from c. p. chloroplatinic acid according to the directions of Adams and Shriner.[11] The reduction was carried out in an apparatus similar to that used by Adams and students[12] in their investigations.

Reduction of Nicotine.—As a standard run 0.1 mole (23.5 g.) of nicotine hydrochloride in 150 cc. of 95% alcohol with 0.2 g. of the platinum-oxide platinum black catalyst was used. The catalyst was not reduced previous to adding the nicotine salt. The time required for complete reduction (absorption of 0.37 mole of hydrogen) varied from three to four hours when the initial pressure of hydrogen gas was 40 pounds per square inch. For the partial reduction (0.30 mole of hydrogen absorbed) two to three hours were required.

When the reduction had been carried to the point desired, the hydrogen was removed and the mixture shaken with oxygen for a short time to coagulate the colloidal catalyst. The catalyst was then removed by filtration and the solvent evaporated as completely as possible under reduced pressure. There is not sufficient difference in the boiling points of the free bases to effect a sharp separation by distillation.

The oily mixture of hydrochlorides was dissolved in a small amount of hot absolute alcohol and acetone was slowly added until the solution just became turbid. Most of the octahydronicotine hydrochloride crystallized on cooling since it is much less hygroscopic and less soluble than either nicotine or hexahydronicotine hydrochlorides; this was removed by filtration. The picrates of the hydrochlorides in the filtrate were formed by adding a saturated alcoholic solution of picric acid. Octahydronicotine picrate is very soluble in alcohol but insoluble in water, hexahydronicotine picrate is soluble in hot but relatively insoluble in cold alcohol, while nicotine picrate is comparatively insoluble in both hot and cold alcohol. The mixed picrates were extracted with hot alcohol on a hot water funnel leaving the nicotine picrate on the funnel and dissolving the hexahydronicotine picrate together with any octahydronicotine present. Upon cooling the filtrate, the hexahydronicotine picrate crystallized and was filtered from the remaining octahydronicotine picrate. By the evaporation of a portion of the alcohol and addition of water, any octahydronicotine which was not previously removed as the hydrochloride was precipitated as the picrate. The hydrochloride of octahydronicotine was recrystallized from absolute alcohol and acetone, the picrate of hexahydronicotine from alcohol. Yields were calculated on the amounts of these recrystallized salts obtained.

The free bases were obtained from the hydrochlorides by treating with sodium hydroxide and extracting with ether. The ether was evaporated and the bases distilled under reduced or atmospheric pressure. To obtain the free bases from the picrates the best procedure was found to be to treat the picrate with a small amount of 20% hydrochloric acid, which hydrolyzed the picrate almost immediately and precipitated a large

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[9] Löffler and Kober, *Ber.*, 42, 3431 (1909).

[10] Pinner, *ibid.*, 27, 1053 (1894).

[11] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

[12] Adams and Voorhees, "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. VIII, 1928, p. 10.

part of the picric acid. This was filtered off and the remainder extracted with ether. The hydrochloride of the base was made strongly basic, the free base extracted with ether and subsequently distilled under reduced or atmospheric pressure.

Reduction of **Metanicotine.**—As a standard run 0.1 mole (23.5 g.) of metanicotine hydrochloride in 150 cc. of 95% ethyl alcohol with 0.2 g. of platinum-oxide platinum black was used. The time required for the reduction to dihydrometanicotine (absorption of 0.1 mole of hydrogen) was thirty minutes, while the reduction to octahydrometanicotine (absorption of 0.4 mole of hydrogen) required three to four hours. The catalyst was removed and the free bases were recovered from the hydrochlorides as in the reduction products of nicotine. The yields are practically quantitative in each case.

The ethylenic linkage in the aliphatic chain in metanicotine is much more easily reduced than the unsaturated bonds in the pyridine nucleus as practically all of the metanicotine is converted into dihydrometanicotine before the reduction of the pyridine ring is started.

Summary

Nicotine hydrochloride has been reduced to a mixture of hexahydronicotine hydrochloride and octahydronicotine hydrochloride with hydrogen using platinum-oxide platinum black as catalyst. Metanicotine hydrochloride has been reduced to both dihydrometanicotine hydrochloride and octahydronicotine hydrochloride, the yields being quantitative.

A method is given for the separation of the reduction products of nicotine involving the solubilities of the hydrochlorides and picrates.

Pure nicotine can be conveniently obtained by crystallization of the hydrochloride from an ether–acetone solution of the commercial 95% nicotine. The hydrochloride recrystallizes from hot absolute ethyl alcohol upon the addition of acetone.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ALABAMA]

SULFUR DYES. I. PREPARATION OF A NEW SERIES[1]

BY GEO. D. PALMER, JR., AND S. J. LLOYD

RECEIVED MAY 20, 1930 PUBLISHED AUGUST 5, 1930

Introduction

In 1861 Troost,[2] by reducing a crude mixture of 1,5- and 1,8-dinitronaphthalenes with sodium sulfide and other reducing agents, obtained colored products. Croissant and BretonniPre[3] obtained a patent in 1873 which included the conversion to dyes of a heterogeneous collection of organic substances (animal and vegetable products, chiefly) when heated with alkali sulfides and polysulfides.

Vidal,[4] in 1893, found that certain aromatic nitrogen compounds yielded

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[1] Presented at the Atlanta meeting of the American Chemical Society, April, 1930.

[2] Troost, *Jahresber,* 958 (1861); cf. French Patent 244,885.

[3] Croissant and Bretonnière, English Patent 1489 (1873).

[4] H. R. Vidal, German Patent 84,632 (1893); St. Dennis and Vidal, German Patent 85,330, etc.

dyes when heated with alkali polysulfides. This discovery directed other investigators into the field of producing sulfur dyes from pure coal tar derivatives. These dyes have proved very valuable. A few examples are Immedial black, from nitro derivatives of hydroxydiphenylamine, and Immedial pure blue and its homologs, from dialkyl-*p*-amino-*p*-hydroxydiphenylamines. Also, many yellow, orange and brown sulfur dyes were obtained by heating toluylene-2,4-diamine and its acyl derivatives with sulfur alone,

The sulfur dyes have yielded practically all colors except bright reds. Reddish shades have been obtained by thionating certain red dyestuffs, such as the azines, rosindulines and safranines. In some cases copper salts were used as catalysts. The brown, blue and black sulfur dyes produce colors which are least affected by light. Hence, the greatest development of the sulfur dye industry has been in the manufacture of dyes producing these colors.

It appears that sulfur dyes have always been produced by heating or fusing various organic substances with sulfur, alkali sulfides, or mixtures of these. Various modifications of this process have been effected, such as boiling an aqueous solution of the organic substance with alkali sulfides or polysulfides, using catalysts, and varying the temperature.

The practical temperatures for the preparation of sulfur dyes range from below 100° to approximately 300°, the vast majority of reactions taking place below 200°. A few sulfur dyes have been prepared by heating above this temperature.[5]

The simplest pure substances used in the preparation of sulfur dyes appear, in the aromatic series, to be *o*-cresol,[6] salicylic acid,[7] nitrophenols, toluidines and aminophenols; in products of animal and vegetable origin, substances of the type of albumin and glucose; in waste products of manufacture, sawdust, cellulose, etc. According to theory, sulfur dyes may be prepared from aromatic nitrogen compounds, or compounds containing phenolic groups.[8]

Vidal succeeded in preparing sulfur dyes from simple pure substances such as p-aminophenol. Wyler[9] obtained a sulfur dye from the aromatic hydrocarbon, acenaphthene, by heating with sulfur at 250–300°. Anthracene,[10] when fused with sulfur at 300°, yields a sulfur vat dye. Retene, when fused with sulfur, forms a sulfur dye. Ellis[11] prepared a sulfur dye

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[5] German Patents 97,285, 118,701, 129,495, 198,049, 161,516; Ö. P. 2336 *Kopp* B., 7, 1746 (1874).

[6] F. Bovini, *Notiz. chim. ind.*, *2*, 688–690 (1927); German Patent 102,897 (1895).

[7] U. S. Patent 909,154 (Jan. 12, 1909).

[8] F. *M*. Rowe, *J. Soc. Dyers Colourists,* **33,** 9 (1917).

[9] M. Wyler, U. S. Patent 1,358,490 (Nov. 9,1921).

[10] Badische Anilin und Soda Fabrik, German Patent 186,990 (March 23, 1906).

[11] *C.* Ellis, U. S. Patent 1,274,351 (July 30, 1918).

from an oxygenated aromatic hydrocarbon, naphthol, by heating with a solution of sodium sulfide and sulfur. Binaphthalene dioxide,[12] fused with sulfur, also forms a sulfur dye. With the exception of these few complicated compounds, it appears that at least two groups must be attached to the benzene ring for sulfur dye formation by all processes used at present, and that, even in the case of cellulose, aromatic substances are formed which subsequently react with sulfur.

Numerous attempts to prepare sulfur dyes from simple organic substances have been made in seeking to determine the structure of the more complicated commercial dyes. Hodgson[13] has directly sulfurated aniline from 160° to the boiling point of aniline, and obtained a small yield of a green complex, insoluble in sodium sulfide. He has obtained similar results **with** o-, m- and *p*-chloro-anilines.[14]

We have found that practically all organic substances in the vapor phase react with sulfur at higher temperatures to form sulfur dyes.

Apparatus and Procedure

In the preparation of these dyestuffs, we proceeded as follows, referring to Fig. **1.**

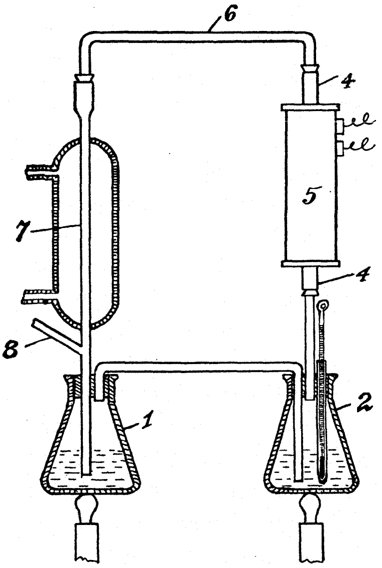

Fig. 1.

The organic material was placed in a vessel, such as flask (1), heated to its boiling point or to a temperature at which the material vaporized, and the vapor passed through the tube as shown, into a vessel (2) containing sulfur heated above its fusing point and above the boiling point of the organic material (preferably to 300° or more.) The bulb of the thermometer was inserted beneath the surface of the sulfur.

The vapors were so introduced as to bubble upward through the molten sulfur, thereby insuring their intimate contact, and hastening the reaction. In the vessel **(2)** the organic vapor combined with the sulfur to form the dyestuff.

Uncombined vapors of the organic compound and gaseous products of the reaction passed through the tube shown, into the tube (4), which is adapted to be heated, as by an electric furnace (5), and from this were carried by means of the tube (6) into a condenser (7), where that portion of the gases which formed liquids or solids at the temperature of the condenser was returned to the flask (1), while that part which remained gaseous escaped through the opening (8), and was collected as desired.

When the organic material was a gas, as ethylene, or acetylene, the flask (1) was.

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[12] I. G. Farbenind. A.-G., Fr. **653,785** (May 1, 1928).

[13] H. H. Hodgson, *J. Chem. Soc.*, **125**, **1855** (1924).

[14] H. H. Hodgson, *J. Soc. Dyers Colourists*, **42**, **82-83** (1926).

of course, not necessary: In the reaction between the organic material and sulfur a considerable quantity of hydrogen sulfide was produced.

With organic compounds such as benzene, alcohol, ether, etc., having a comparatively low boiling point, the furnace (5) was not necessary. In the case of a solid, such as anthracene, or naphthalene, having a comparatively high boiling point, the furnace prevents the condensation of the solid in the connecting tubes.

On the completion of the reaction, the material in flask (2) was removed and pulverized. This pulverized mass was washed with carbon bisulfide until all free sulfur was dissolved out.

Three hundred grams of organic substance, such as benzene or toluene, was placed in flask (1) and two hundred grams of flowers of sulfur in flask (2). These were heated for several hours. In some cases the operation was continued until hydrogen sulfide ceased to be given off. Our procedure consisted of first heating the sulfur to approximately 380°, then allowing the vapor of the organic substance to bubble slowly through the sulfur. The heat was so regulated that a constant drip of excess organic substance could be observed in the condenser. The hydrogen sulfide was allowed to bubble into an excess of lead acetate solution; the lead sulfide was washed, dried and weighed, and the corresponding amount of hydrogen sulfide calculated. The dye formed and the sulfur and organic substance remaining were weighed. From these weights the ratio of sulfur in hydrogen sulfide to sulfur in the dye, and the amount of organic substance used were determined. The dyes were analyzed for sulfur.

Results

Apparently, all types of organic substances, when vaporized and passed over or through molten sulfur above 300°, formed sulfur dyes in good yields, practically without carbonization. Better yields were obtained at approximately 380°. They are true sulfur dyes in the sense that they dissolve in an aqueous solution of sodium sulfide, and dye cotton, rayon and other vegetable fibers directly. Apparently these dyes are not oxidized in the dyeing process, as the color of the dyed skein is approximately the same as that of the aqueous sodium sulfide solution of the dye. The dye dissolved in aqueous sodium sulfide may be precipitated upon addition of acid, and redissolved in aqueous alkali sulfide solution.

Sulfur dyes of various colors were prepared by passing separately the vapors of pure benzene, toluene, aniline, phenol, benzaldehyde, naphthalene, anthracene, diphenyl, chlorobenzene, dichlorobenzene, diethylaniline, furfural, acetic acid, ethyl alcohol, ether, kerosene and turpentine over, or through, molten sulfur above 300°, preferably between 350 and 400". Sulfur dyes were also obtained from ethylene, acetylene and by-product gases when these were passed over or through sulfur under the same conditions. The colors of all the dyes are specific and easily reproduced. They are fast to repeated washings with soap and water, and to all organic solvents of which we are aware. In fact, most of the properties are those of sulfur dyes prepared in the usual manner.

Discussion

Through this process we have prepared sulfur dyes which give to vegetable fibers all colors except distinct reds, yellows, blues and blacks.

Undoubtedly many of these colors will later be produced, as many other substances are yet to be tried.

In Table I it appears that the reddish color of these sulfur dyes is connected with the benzene ring. On rayon the benzene sulfur dye gives a red color with very little brown. The replacement of a hydrogen atom of a benzene ring by an amino group makes a great change in color.

TABLE I

SUBSTANCES VAPORIZED THROUGH SULFUR

		Color on cotton and rayon
Benzene	↑	Reddish-brown
Naphthalene		Reddish-brown
Anthracene		Reddish-brown
Dichlorobenzene		Reddish-brown
Monochlorobenzene		Reddish-brown
Furfural		Reddish-brown
Ethylene		Reddish-brown
	Toward Red	
Carbolic acid		Brown
Benzaldehyde		Brown
By-product gas		Brown
Diethyl ether		Grayish-brown
Ethyl alcohol (abs)		Grayish-brown
Acetylene		Gray
	Toward Green	
Kerosene		Khaki
Turpentine		Khaki
Diethylaniline		Khaki
Acetic acid		Khaki
Diphenyl		Khaki
Toluene	↓	Khaki
Aniline		Green

It is of interest to know that carbon tetrachloride, when passed through sulfur under conditions for dye formation, failed to yield a dye. Dye formation appears to be directly proportional to the amount of hydrogen sulfide evolved. Hence, it would appear that hydrogen-containing organic compounds are necessary to produce sulfur dyes when passed through or over sulfur at 300° or more.

We have always found that a definite relationship exists between the amount of hydrogen sulfide evolved and the amount of dye formed. In Table II, in the case of the benzene sulfur dye, for every one atom of sulfur that went into dye formation, one atom of sulfur was evolved as hydrogen sulfide. In the case of the toluene sulfur dye, Table III, for every three atoms of sulfur that went into dye formation, two atoms of sulfur were evolved as hydrogen sulfide.

It also appears that for every five molecules of benzene that went into dye formation, eight atoms of sulfur reacted. Apparently no appreciable amounts of by-products are formed in the benzene and toluene sulfur dyes. By-products have been obtained in other cases. It is quite likely that the weights of benzene used are too high, owing to loss of benzene by volatilization. Therefore, the benzene–sulfur ratio should not be regarded as significant in this case. In a similar manner, for each molecule of toluene that went into dye formation, five atoms of sulfur reacted. No appreciable amount of toluene was lost by volatilization. The following reaction appears to take place: $[C_6H_5CH_3 + 5S \longrightarrow \text{Dye (3S)} + 2H_2S]_x$. The sulfur in hydrogen sulfide evolved, subtracted from the total sulfur reacted (obtained by weighing all sulfur throughout the reaction) is identical with the sulfur in dye obtained by multiplying the weight of pure dye by percentage sulfur.

TABLE II

BENZENE SULFUR DYE (370–390°)

No.	Time Hours	Min.	Benzene, g.	Sulfur, g.	Benzene to sulfur ratio	Dye formed, g.	Sulfur, in dye. %	g.	Sulfur in H_2S, g.	Ratio of Sulfur in dye to sulfur in H_2S
1	1	32	35.4	23.0	1.54:1	15.5	63.40	9.8	10.3	1:1
2	4	21	38.3	24.9	1.54:1	19.2	65.25	12.5	10.8	1:1
3	4	27	38.2	23.4	1.63:1	17.0	64.40	11.0	10.6	1:1
4	6	34	45.9	29.3	1.56:1	23.0	64.50	14.8	14.9	1:1
5	12	23	41.4	26.5	1.56:1	21.4	66.10	14.0	11.2	1:1
Av.					3:2 g.					1:1 g.
Av.					5 moles:8 g. atoms		64.73			1:1 g. atoms

TABLE III

TOLUENE SULFUR DYE (370–390°)

No.	Time, Hours	Min.	Toluene, g.	Sulfur, g.	Toluene to sulfur ratio	Dye formed, g.	Sulfur in dye, %	g.	Sulfur in H_2S, g.	Ratio of sulfur in dye to sulfur in H_2S
1	4	30	16 4	26.5	1:1.61	24.3	64 38	15.6	9.8	3:2
2	5	0	20 9	38 3	1:1.83	32.0	63.00	20.2	13.4	3:2
3	6	0	23.6	37 4	1:1.60	34.4	63.87	22.0	13.7	3:2
4	13	0	37.4	61.7	1:1.65	52.7	64.50	34.0	20.0	3:2
Av.					1:1.67 g.					3:2 g.
Av.					1 mole:5 g. atoms		63 93			3:2 g. atoms

From Tables II and III it may be noted that the percentage of sulfur in dye remains fairly constant for each dye (benzene and toluene), regardless of the length of the run. The small differences in different runs are undoubtedly due to slight amounts of carbon formed in some runs. Also, the sulfur analysis of the benzene sulfur dye prepared at the boiling point of sulfur (444°) is identical with that of the benzene sulfur dye prepared at 380". The colors of these dyes on rayon and cotton skeins are constant, regardless of the time and temperature of preparation. The twenty sulfur dyes that we have prepared (Table IV) represent practically all types of organic compounds. From the percentages of sulfur in the dyes prepared from aromatic substances, it appears that each benzene ring is attached to four or five sulfur atoms. This seems to be true in the case of most of the benzene derivatives used.

TABLE IV

COLORS AND SULFUR ANALYSES

Dye	Color of solid dye	Percentage of sulfur Found		Av.
Benzene	Brick red	64.60	64.84	64.72
Naphthalene	Brick red	71.40	71.10	71.25
Anthracene	Blackish-red	72.91	73.13	73.02
p-Dichlorobenzene	Orange	73.96	74.11	7403
Monochlorobenzene	Reddish-brown	73.52	72.90	73.21
Furfural	Bluish-black	80.20	80.37	80.28
Ethylene	Bluish-black	61.54	61.15	61.34
Carbolic acid	Bluish-black	63.76	64.25	64.00
Benzaldehyde	Bluish-black	63.51	63.46	63.48
Ethyl alcohol (abs.)	Gray	10.13	9.56	9.84
Acetylene	Bluish-black	68.15	67.85	68.00
Kerosene	Bluish-black	61.98	61.78	61.88
Turpentine	Greenish-black	62.64	62 29	62.46
Diethylaniline	Bluish-black	60.30	60.12	60.21
Acetic acid	Bluish-black	49.47	49.61	49 54
Toluene	Greenish-brown	63.58	63.99	63.78
Aniline	Green	58.60	58.00	58.30

We hesitate to attempt to write the structure of these sulfur dyes until we have more data. The high sulfur content appears to show that chains of sulfur atoms must be attached to the benzene, toluene, etc., rings.

Probably a chromophore group, consisting of sulfur atoms in certain formations, exists. The colors of the dyes are apparently modified by various groups which are attached to such a chromophore.

Many hydrocarbons[15] heated with sulfur have yielded various non-dye substances. Ziegler,[16] in 1890, stated that the stability of the benzene ring toward sulfur is remarkable, and that certain basic groups attached to the benzene nucleus are necessary for reactivity with sulfur. Szperl[17] succeeded in reacting sulfur with benzene in a sealed tube. He obtained non-dye substances in which the sulfur was not substituted for hydrogen of the benzene ring. Glass and Reid[18] have shown that sulfur can be introduced

[15] V. Meyer and Sandmeyer, *Ber.*, 16,2176 (1883); E. Baumann und E. Fromm, *ibid.*, *28*, 890–895, 895–907, 907–914 (1895); a review of the literature of the subject, Ludwik Szperl, *Chemik Polski*, 15, 8–10 (1917).

[16] J. H. Ziegler, Ber., 23, 2472 (1890).

[17] Ludwik Szperl, *Roczniki Chem.*, 6, 155 (1926).

[18] H. B. Glass and E. Emmet Reid, THIS JOURNAL, **51**, 3428 (1929).

directly into aromatic hydrocarbons, such as benzene and ethylbenzene, without catalysts, in a steel bomb at 350°. Thiophenol was produced from benzene and sulfur along with other related sulfur compounds. This work suggests that the brownish-red dye which we have obtained by passing the vapor of benzene over or through molten sulfur at atmospheric pressure is prepared through the mechanism of thiophenol formation.

In the case of aniline and sulfur, we obtained a green dye, soluble in an aqueous solution of sodium sulfide. Hodgson's work[19] indicates, at least in the case of aniline, that our process of using the vapor of the organic substance in contact with sulfur at high temperatures give to the sulfurated substance the property of solubility in an aqueous solution of sodium sulfide.

We have substituted selenium for sulfur in the above process, and have obtained similar reactions.

The production of a sulfur dye in this simple manner from substances such as benzene and ethylene naturally arouses the hope that definite ideas on the structure of sulfur dyes may shortly be obtained. Work directed to this end is now proceeding in the laboratory of the University.

Summary

1. Practically all types of hydrogen-containing organic compounds, such as benzene, toluene, furfural, ethylene, ether, kerosene, etc., when vaporized and passed over or through molten sulfur above 300°, form true sulfur dyes in good yields, practically without carbonization.

2. Twenty dyes, which give to vegetable fibers all colors except distinct reds, yellows, blues and blacks, have been prepared.

3. Sulfur analyses, ratios of sulfur in dyes to sulfur in hydrogen sulfide evolved, and ratios of organic substances to sulfur reacted are given.

4. Some ideas as to the structures of the sulfur dyes prepared from these simple substances are presented.

UNIVERSITY, ALABAMA

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[19] H. H. Hodgson, *J. Chem. Soc.*, **125**, 1855 (1924); *J. Soc. Dyers Colourists*, **42**, 82–83 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

A NUCLEAR SYNTHESIS OF UNSATURATED HYDROCARBONS.
I. ALPHA-OLEFINS[1,2]

BY HARRY B. DYKSTRA, J. FRANKLIN LEWIS AND CECIL E. BOORD

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In a recent paper by Lloyd C. Swallen[3] and one of us, a method was suggested for the synthesis of olefins. This method has been developed and perfected to the point where it now promises to be of real service in the study of unsaturated hydrocarbons. The necessity for revision and extension of our knowledge of these hydrocarbons has frequently been pointed out.[4] This necessity arises not only from the increasing industrial use of these compounds but also from the fact that much of the previous literature has been found to be in error.

The more recent investigations in so far as they relate to a-olefins give boiling points lower than those previously given. Brochet,[5] Schorlemmer,[6] and Norris and Joubert[7] give 39–40° as the boiling point of pentene-1. On the other hand, Kirrmann[8] and Bourguel[9] give 30.5–31" and 32.5°, respectively. Brochet[S] gives 67" and van Beresteyn[10] 67.7–68.1° as the boiling point of hexene-1, while Brooks and Humphrey[1'] give 60.5–61.5° and Miss van Risseghem[12] gives 63.35" ± 0.05° for the same compound. These variations are merely indicative of a confusion which is somewhat general in the literature of unsaturated hydrocarbons.

The differences in results obtained by different investigators may be attributed to a number of sources. As Brooks[13] has said: "High temperatures and many chemical reagents, particularly acids, cause such *a*-olefins to rearrange or the double bond to shift its position. Only re-

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Presented in part before the division of Organic Chemistry at the meeting of the American Chemical Society in Detroit, Michigan, September 8, 1927.

[2] This paper is abstracted from the Dissertation of Harry B. Dykstra and in part from the Dissertation of J. Franklin Lewis as presented in partial fulfilment of the requirements of the degree of Doctor of Philosophy, to the Faculty of the Graduate School of The Ohio State University, June, 1927, and March, 1930, respectively.

[3] Swallen and Boord, THIS JOURNAL, **52**, 651 (1930).

[4] Brooks, "Non-Benzenoid Hydrocarbons," The Chemical Catalog Company, New York, 1922, p. 158.

[5] Brochet, *Bull. soc. chim.*, [3] **7**, 567 (1892).

[6] Schorlemmer, *Ann.*, **161**, 269 (1872).

[7] Norris and Joubert, THIS JOURNAL, **49**, 873 (1927).

[8] Kirrmann, *Bull. soc. chim.*, **39**, 988 (1926).

[9] Bourguel, *ibid.*, **41**, 1475 (1927).

[10] Van Beresteyn, *Bull. soc. chim. Belg.*, **25**, 293 (1911).

[11] Brooks and Humphrey, THIS JOURNAL, **40**, 833 (1918).

[12] Van Risseghem, *Bull. soc. chim. Belg.*, **35**, 328 (1926).

[13] Ref. 4, p. 178.

actions employing low temperatures and the absence of isomerizing agents can be expected to produce a-olefins in any degree of purity. . ."

The preparation of a-olefins by low-temperature methods involves difficulties of another type. The condensation of an alkylmagnesium halide with allyl bromide in so far as it has been applied to the preparation of pentene-1[3,8] and hexene-1[11,12] introduces the necessity of purifying these products from the alkyl halides and ethers used in the condensation. The purification processes are long and tedious and are not always wholly successful. The reduction of the corresponding acetylene to an olefin by hydrogen in the presence of a catalyst[10] involves the inherent possibility of the simultaneous formation of the corresponding saturated hydrocarbon.

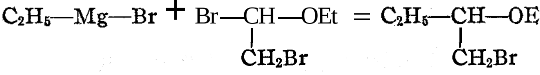
The synthesis described in this paper is not entirely free from such difficulties. The products prepared have the usual olefin characteristics in that they are not directly obtained in a high degree of purity. The method does, however, seem to yield products possessing the structure indicated by the synthesis.

No attempt has been made in the present work to apply the high degree of refinement used by Miss van Risseghem[12] in her excellent work on hexene-1 and hexene-2. Work of this character requires the production of several hundred grams of each product. The process described will ultimately lend itself to such studies. For the present our efforts have been confined to the perfection of the method and a description of those products which have not yet been adequately described.

The nuclear synthesis is a four step process. The first three steps lead to the preparation of a series of β-ethoxy-alkyl bromides (β-bromo ethers). Its application to the synthesis of pentene-1 is shown by the following scheme

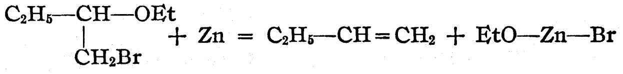
$$\mathrm{CH_3{-}CHO + EtOH + HCl = CH_3{-}CHCl{-}OEt + H20} \qquad (1)$$

$$\mathrm{CH_3{-}CHCl{-}OEt + Br_2 = CH_2Br{-}CHBr{-}OEt + HCl} \qquad (2)$$



$$\mathrm{C_2H_5{-}Mg{-}Br + \underset{\displaystyle CH_2Br}{Br{-}\underset{|}{C}H{-}OEt} = \underset{\displaystyle CH_2Br}{C_2H_5{-}\underset{|}{C}H{-}OEt} + MgBr_2} \qquad (3)$$

In the fourth step zinc is used for the simultaneous removal of the ethoxy group and bromine in a manner similar to that used by Gladstone and Tribe[14] for regenerating an olefin from its dibromide.



$$\begin{matrix}\mathrm{C_2H_5{-}CH{-}OEt}\\ |\\ \mathrm{CH_2Br}\end{matrix} + \mathrm{Zn} = \mathrm{C_2H_5{-}CH{=}CH_2 + EtO{-}Zn{-}Br} \qquad (4)$$

It has been found advisable to avoid fractionation of the halogenated ethers obtained in steps one and two because of loss in yield by decomposition. The β-bromo ethers obtained in step three are quite stable and may be completely purified. The formation of the olefin in step four is slow but the yields are satisfactory.

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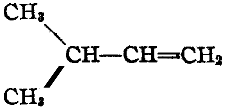
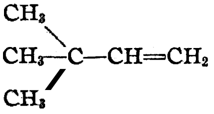
[14] Gladstone and Tribe, *Ber.*, 7,364 (1874); *J. Chem. Soc.*, 21,306 (1878).

Pentene-1, hexene-1, 4-methylpentene-1 (iso-α-hexene) and 5-methylhexene-1 (iso-α-heptene) have been prepared by the scheme outlined above. Of these the iso-a-hexene seems not to have been described previously. The other three were obtained with boiling points agreeing closely with those given for the same compounds when prepared by other low-temperature methods. Since Kirrmann on the one hand and Norris and Joubert on the other did not obtain the same results in the synthesis of pentene-1 by the action of ethylmagnesium bromide upon allyl bromide, this condensation has been carefully repeated a number of times. In every case, regardless of the method of purification used, a product boiling at 29–31° was obtained.[15]

By combining steps three and four in the synthesis it has been possible to condense allyl bromide with α,β-dibromo-ethyl ether and to produce the heretofore unknown 1,4-pentadiene. This compound was purified by conversion into its crystalline tetrabromide, the diene being regenerated by the action of zinc on an alcoholic solution.

Some of the more recently determined values for the boiling points of the α-olefins, including those contained in the present paper, are shown in Table I for comparison with those of the corresponding β-olefins and saturated hydrocarbons. It will be noted that the boiling point of 1,4-pentadiene is lower than that of pentene-1 and this is in turn lower than that of n-pentane. Also that of 1,5-hexadiene is lower than that of hexene-1 and this is lower than n-hexane. Further, it will be noted that the boiling point of iso-α-pentene is lower than for isopentane, iso-α-hexene lower than isohexane and iso-a-heptene lower than isoheptane. From these facts one may tentatively formulate the following rule: an a-olefin of the type $R—CH = CH_2$ boils lower than the corresponding saturated hydrocarbon. The usual branching chain rule with respect to boiling points may be restated for olefins as follows: in any given family of *olefins the* one *having* the *most* highly branching chain substituted on the ethylene *group* ($— CH = CH_2$) *has* the lowest boiling point. Combining the two rules one sees that isopropylethylene, I, should be the lowest boiling of the pentenes and tertiary butylethylene, II, the lowest boiling hexene. An examination of the literature shows this to be the case.


I


II

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[15] **Dr. Mary L. Sherrill, of Mount Holyoke College, in a private communication, states that she also has prepared pentene-1 by the above method using the Kirrmann procedure. The product obtained had the following physical constants: m. p. (754 mm.) 30.5–31.0°; *d* 0.6419; n^{20}_{D} 1.3711.**

Further examination of Table I shows that the boiling point of pentene-1 is lower than that of pentene-2, hexene-1 lower than hexene-2 and iso-α-hexene lower than iso-β-hexene.

TABLE I

BOILING POINTS OF α-OLEFINS

Hydrocarbon	B. p., °C.	Investigator
$CH_3-CH_2-CH_2-CH_2-CH_3$	36.3	Thorpe and Jones"; Young[b]
$CH_3-CH=CH-CH_2-CH_3$	36.4	Sherrill, Otto and Pickett[c]
	36.39	Norris and Reuter[d]
$CH_2=CH-CH_2-CH_2-CH_3$	30.5–31	Kirrmann[e]
	32.5	Bourguel[f]
	29.5–31, 30 2	Present paper
$CH_2=CH-CH_2-CH=CH_2$	29–30	Present paper
$CH_3-CH_2-CH(CH_3)_2$	27.95	Young and Thomas[B]
$CH_2=CH-CH(CH_3)_2$	20.5–20.7	Michael and Zeidler[h]
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$	68.95	Young[i]
$CH_3-CH=CH-CH_2-CH_2-CH_3$	68.0–68 2	van Risseghem[k]
$CH_2=CH-CH_2-CH_2-CH_2-CH_3$	63.35	van Risseghem
	61–64	Present paper
$CH_2=CH-CH_2-CH_2-CH=CH_2$	59.57	Cortese"
$CH_3-CH_2-CH_2-CH(CH_3)_2$	60.2	van Risseghem[m]
$CH_3-CH=CH-CH(CH_3)_2$	58.15–59 15	van Risseghem
$CH_2=CH-CH_2-CH(CH_3)_2$	53–59	Present paper
$CH_3-CH_2-C(CH_3)_3$	49.6–49.7	Markownikow[n]
$CH_2=CH-C(CH_3)_3$	41.2	Delacre[o]
$CH_3-CH_2-CH_2-CH_2-CH(CH_3)_2$	89.9–90.4	Francis and Young[P]
$CH_2=CH-CH_2-CH_2-CH(CH_3)_2$	84–85	Brooks and Humphrey[y]
	85–86	Andre'
	84–86	Present paper

[a] Thorpe and Jones, *J. Chem. Soc.*, 63, 290 (1893); [b] Young, *ibid.*, 71, 446 (1897); [c] Sherrill, Otto and Pickett, THIS JOURNAL, 51, 3023 (1929); [d] Norris and Reuter, *ibid.*, 49, 2632 (1927); [e] Kirrmann, *Bull. soc. chim.*, 39, 988 (1926); [f] Bourguel, *ibid.*, 41, 1475 (1927); [g] Young and Thomas, *J. Chem. Soc.*, 71,440 (1897); [h] Michael and Zeidler, Ann., 385, 250 (1911); [i] Young, *J. Chem. Soc.*, 73, 906 (1898); [k] van Risseghem, *Bull. soc. chim. Belg.*, 35, 328 (1926); [l] Cortese, THIS JOURNAL, 51, 2268 (1929); [m] van Risseghem, *Bull. soc. chim. Belg.*, 30, 8 (1921); [n] Markownikow, *Ber.*, 32, 1446 (1899); [o] Delacre, *Bull. acad. roy. med. Belg.*, 7 4 1 (1906); [p] Francis and Young, J. Chem. *Soc.*, 73,906, 922 (1898); [q] Brooks and Humphrey, THIS JOURNAL, 40,834 (1918); [r] André, Ann. *chim. phys.*, [8]29,554 (1913).

Experimental Part

The Preparation of β-Bromo Ethers

A. **Alkyl-α-chloro-ethyl** Ether, $R-O-CHCl-CH_3$.—The method described by Swallen and one of us[3] has been generalized and extended to include the preparation of n-propyl- and n-butyl-a-chloro-ethyl ethers. It was found advisable for the purpose of synthesis to avoid distillation, the yield being diminished as much as 20 to 25% by a single fractionation. The reaction mixture separates into two layers. The upper ethereal layer is removed and dried over calcium chloride. For the α-chloro-ethyl ethers mentioned above the yield varies from **80** to 90% of crude or **60** to **69%** of the distilled product.

B. **Alkyl-α,β-dibromo-ethyl** Ethers, R—O—CHBr—CH_2Br.—The alkyl-α-chloro-ethyl ethers were brominated by the procedure previously described. The crude reaction products may be submitted directly to distillation under diminished pressure but it was found advisable in this case also to avoid distillation. The hydrogen chloride was removed under diminished pressure or by aspirating a slow current of air through the reaction mixture. The yields vary from **93** to **95%** of crude or **88.5** to **91%** of distilled product. The physical constants and analyses of ethyl-, n-propyl- and *n*-butyl-α,β-dibromo-ethyl ethers are shown in Table **II.** The last two ethers have not been described previously.

TABLE II

α,β-DIBROMO-ETHYL ALKYL ETHERS, R—O—CHBR—CH_2BR

α,β-Dibromo-ethyl (*Alkyl*) Ethers	Yield, %	B. p., °C.	d^{20}_{20}	Analyses, Br, % Found	Calcd.
Ethyl	**90.5**	**86 (31** mm.)	**1.7370**	**68.89**	**68.92**
n-Propyl	**92.9**[a]	**97 (27 mm.)**	**1.6554**	**64.92**	**64.99**
n-Butyl	**95.2**[a]	**115 (36** mm.)	**1.5647**	**61.15**	**61.49**

[a] These yields are for crude products as used in the synthetic experiments.

Wislicenus, who[16] obtained the ethyl derivative by brominating the vinyl ethyl ether, says "it is not possible to obtain the pure product by fractional distillation since it decomposes upon heating with the evolution of hydrogen bromide and the formation of a black non-volatile tar." The analyses given in Table **II** are those obtained for the products after a single distillation. Repeated distillations tend to produce a lowering of the boiling point by decomposition.

C. **Alkyl-β-Bromo-ethyl** Ethers, **Condensation** of **α,β-Dibromo-ethyl** Ether with an **Alkylmagnesium** Halide.—In the earlier experiments the coupling was effected by adding the ether solution of the Grignard reagent to an anhydrous ether solution of the dibromo ether, in order to avoid the presence of residual magnesium. It was soon found that the products prepared in this way were difficult to purify. Since an excess of the alkylmagnesium halide increased both the yield and purity of the product, the later experiments were carried out using the same order of mixing the reagents that was used by Houben and **Führer.**[17]

The Grignard reagents were made in the usual manner. The flask was surrounded by ice water and the dibromo ether, dissolved in an equal volume of anhydrous ether, added through the dropping funnel at such a rate that the mixture remained cold. Mechanical stirring was used throughout and for fifteen minutes after the addition was completed. The reaction mixture was decomposed by pouring on ice and acidifying with dilute hydrochloric acid. The ether layer was separated, dried over calcium chloride, and the ether removed by distillation. The product was then transferred to a smaller flask, about 5% of its weight of solid sodium hydroxide added, and fractionated. **β-Ethoxy-*n*-propyl** bromide and **β-ethoxy-*n*-butyl** bromide may be distilled at atmospheric pressure but the higher members are best distilled under diminished pressure. The yields, physical constants and analyses of fourteen **β-bromo** ethers prepared by this procedure are given in Table **III.** The yields recorded in the table are those obtained after a single distillation and are calculated on the basis of the dibromo ether used.

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[16] Wislicenus, Ann., **192,111 (1878).**

[17] Houben and **Führer,** *Ber.*, **40,4993 (1907).**

TABLE III

β-ALKOXY-ALKYL BROMIDES, R—O—CHR′—CH_2Br

Alkyl	R'	Yield, %	B. p , °C.	d_{20}^{20}	Analyses, found	Br, % calcd.
			β-Ethoxy (alkyl) bromides			
n-Butyl[a]	C_2H_5-	62	67 (34 mm.)	1.2312		
n-Amyl"	*n*-C_3H_7-	57	82 (34 mm.)	1.1812		
n-Hexyl[a]	*n*-C_4H_9-	81	98–99 (33 mm.)	1.1548		
Isohexyl	iso-C_4H_9-	46	89–92 (38 mm.)	1.1578	37.66	38.23
Isoheptyl"	iso-C_5H_{11}	65	106–109 (33 mm.)	1.1209		
			β-Propoxy (alkyl) bromides			
n-Propyl	CH_3-	61	65 (32 mm.)	1 2205	44.17	44.15
n-Butyl	C_2H_5-	73	66 (15 mm.)	1.1803	40.97	40.98
n-Amyl	*n*-C_3H_7-	70	81–82 (13 mm.)	1.1439	38.25	38.23
Isoamyl	iso-C_3H_7-	34	77–78 (14 mm.)	1.1349	37.84	38.23
n-Hexyl	*n*-C_4H_9-	81	92–93 (14 mm.)	1.1226	35.81	35.83
Isoheptyl	iso-C_5H_{11}-	58	112–114 (28 mm.)	1.0872	33.54	33.71
Phenylethyl	C_6H_5	72	123 (12 mm.)	1.2518	33.05	32.88
			β-Butoxy (alkyl) bromides			
Isoheptyl	iso-C_5H_{11}-	65	127–128 (27 mm.)	1.0686	31.88	31.82

[a] Swallen and Boord, THIS JOURNAL, 52, 655 (1930).

Synthesis of Olefins.—For conversion into the olefin the β-bromo ether was dissolved in approximately two and one-half times its volume of 90% alcohol and placed in a three-necked flask under a spiral condenser. The flask was provided with a mechanical stirrer having a mercury seal. From two to three equivalents of zinc dust were added and the reaction mixture digested at the boiling point for several hours.

The lower bromo ethers decomposed more slowly than those of higher molecular weight. β-Ethoxy-*n*-amyl bromide yielded 60–65% of the crude pentene by treatment for ten to twelve hours, while β-ethoxyisoheptyl bromide gave a yield of 85–90% of isoheptene in five hours. The zinc dust tends to become coated with the basic salt produced. Mechanical stirring serves to obviate this difficulty in part and there is some advantage in adding the zinc portion-wise.

The separation of the olefin from the reaction mixture differed slightly, depending upon its boiling point. In the case of a-pentene the water in the spiral condenser was kept at 40° so that the olefin volatilized from the reaction mixture continuously. The vapors were condensed by leading through a trap immersed in a freezing mixture. In case of the higher olefins the reflux condenser was replaced from time to time by a Hempel column and the product together with a portion of the alcohol distilled off. More alcohol was then added and the digestion continued.

The alcoholic distillates collected in this way were diluted with an equal volume of cold water. The upper layer of olefin was separated, washed with water and dried over calcium chloride. The yields of crude olefins prepared are shown in Table IV.

TABLE IV

α-OLEFINS

β-Alkoxyalkyl bromide	Grams used	Olefin	Yield, %	B. p., °C.	d_{20}^{20}
β-Ethoxy-*n*-amyl	98	$CH_3(CH_2)_2CH{=}CH_2$	65	29.5–31.0	0.6465
β-Propoxy-*n*-amyl	105	$CH_3(CH_2)_2CH{=}CH_2$	57	....	...
β-Ethoxy-*n*-hexyl	150	$CH_3(CH_2)_3CH{=}CH_2$	80	61–64	.6784
β-Ethoxyisohexyl	105	$(CH_3)_2CH{-}CH_2{-}CH{=}CH_2$	60	52.5–54.5	.6718
β-Ethoxyisoheptyl	56	$(CH_3)_2CH(CH_2)_2CH{=}CH_2$	90	84-86	.6956

The products prepared by the above procedure, like those prepared by other methods, do not have as sharp a boiling range as could be desired. Much larger quantities will need to be prepared before they can be obtained in a high degree of purity. Long standing over calcium chloride tends to increase polymerization. Usually about 60% of the crude product distilled with a boiling range of two degrees. Particular difficulty was experienced in the case of iso-a-hexene because of the character of the isobutyl bromide available for the preparation of the corresponding β-bromo ether. The observed boiling points and gravities are also shown in Table IV.

Olefin Dibromides.—From 10 to 15 cc. of each of the olefins described was dissolved in four times its volume of anhydrous ether and cooled in a freezing mixture. An equivalent quantity of bromine was added dropwise with stirring. The bromine was absorbed rapidly and quantitatively. The ether was then evaporated and the dibromo paraffins distilled under diminished pressure. The yields were nearly quantitative.

Analyses for bromine by the Drogin–Rosanoff[18] method were always too low. The error for the lower members was greater than for those of higher molecular weight and in some cases equaled several per cent. Resort to the Carius method showed the compounds to be correctly represented as the dibromides of the olefins indicated in each case. The physical constants and analyses are indicated in Table V.

TABLE V

OLEFIN DIBROMIDES

Formula	B. p., °C.	d^{20}_{20}	Analyses, found	Br, % caicd.
$n\text{-}C_3H_7CHBr\text{-}CH_2Br$	84–85 (32 mm.)	1.6525	69.59	69.52
$n\text{-}C_4H_9CHBr\text{-}CH_2Br$	103–105 (36 mm.)	1.5632	65.19	65.53
iso-$C_4HC_9HBr\text{-}CH_2Br$	96–99 (38 mm.)	1 5507	65.46	65.53
iso-$C_5H_{11}CHBr\text{-}CH_2Br$	110–113 (34 mm.)	1.4913	61.55	61.95

Synthesis of Pentene-1 by the Action of Ethylmagnesium Bromide upon Allyl Bromide.—Twenty-four grams of magnesium was covered with 160 cc. of anhydrous ether and treated with 108 g. of ethyl bromide. To the ether solution of the ethylmagnesium bromide, cooled in ice water, 120 g. of allyl bromide was added during a period of three hours and the reaction mixture allowed to stand overnight. One hundred twenty grams of distillate was collected by heating the reaction mixture over the water-bath and the product so obtained purified by a procedure essentially as described by Norris and Joubert.[7] It was digested at its boiling point with three grams of finely divided metallic sodium for one and three-quarter hours. Three grams more sodium was added and the digestion continued for three hours longer. The product was then removed from the sodium by decantation, 10 g. of magnesium turnings added and the digestion continued for fifteen hours. Distillation yielded 75 cc. of a distillate which was washed five times with 30-cc. portions of a mixture of equal *parts* of concentrated and 6 N hydrochloric acid. It was then washed ten times with 25-cc. portions of cold water. The moist oily layer, which now weighed 29.5 g., was dried over metallic sodium and fractionated with the following results: 30–33', 13 g.; 33–36', 9 g.; 3641', 2.1 g.; 41–51°, 1.3 g.

One hundred and eighty cc. of the pentene collected from three condensations in which a total of five moles of the reactants had been used was purified and fractionated using an eight inch Midgley[19] column. A small portion distilling at 28.5" was probably isopentane.[20] The principal fraction totaled 90 cc. and distilled at 29.6–30.8' (mostly

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[18] Drogin and Rosanoff, THIS JOURNAL, 38, 711 (1916).

[19] Midgley, Ind. Eng. *Chem. (Anal.* Ed.), 1, 86 (1929).

[20] The presence of isopentane is readily accounted for if one assumes that allyl bro-

at 30.1°) under 747 mm. pressure. The residue in the flask still carried a distinct odor of ether. An Engler distillation curve run on the principal fraction showed its purity not yet wholly satisfactory but indicated a boiling point of 30.2" under 747.8 mm. pressure.

Purification of Pentene-1 through its Dibromide.—The condensation of ethylmagnesium bromide with allyl bromide was repeated using one half molar quantities, Purification was effected by converting the pentene into its dibromide, which was fractionated and the olefin regenerated by the action of zinc dust and alcohol. Sixteen and one-half cc. of bromine was required to saturate the ether solution of the pentene obtained. Fractionation yielded 59 g. of a dibromide boiling at 90–96° under 40 mm. Forty grams of zinc dust was covered with 130 cc. of alcohol and the dibromide added in small portions. The heat developed by the addition of each portion was allowed to subside before a new portion was added. After the addition was completed the reaction mixture was submitted to distillation which began at 27° and was continued up to the boiling point of alcohol. Dilution of the distillate with a large volume of cold water yielded 11.2 g. of the olefin which, after drying over calcium chloride, distilled entirely at 29–31°.

Synthesis of 1,4-Pentadiene

Preparation of 1,4-Pentadiene Tetrabromide, $CH_2Br{-}CHBr{-}CH_2{-}CHBr{-}CH_2Br$.—A mixture of 180 g. of allyl bromide and 302 g. of α,β-dibromo-ethyl ether was dropped slowly onto 75 g. of magnesium covered with 600 cc. of anhydrous ether. The reaction mixture was vigorously stirred and kept cold in an ice-bath. Although an energetic reaction took place, the mixture did not darken, as is the case when the dibromo ether alone is treated with magnesium. After the reaction was completed the mixture was poured onto cracked ice, the ether layer separated, dried over calcium chloride and distilled. That portion passing over below 60° and containing both the pentadiene and ether was cooled and treated with bromine until no more was absorbed. One hundred and twelve grams (35 cc.) of bromine was required. The ether was removed by distillation and the product allowed to stand. After twenty-four hours the residue had partially crystallized and was filtered by suction. The crystalline product weighed 39 g. and the non crystalline portion 58 g. After washing with cold alcohol the crystalline tetrabromide melted at 78–82°. Recrystallization from alcohol yielded a product melting at 84–87°. Demjanow and Dojarenko[21] give 86° as the melting point of 1,4-pentadiene tetrabromide. Diallyl tetrabromide is described[22] as melting at 63°.

In six runs, involving a total of $9^{2}/_{3}$ moles of the dibromo ether, 270 g. of crystalline tetrabromide was obtained. The magnesium consumed varied from 70 to 96% of the theoretical. The bromine absorbed indicated a crude yield of unsaturated product of from 28 to 38% based upon the magnesium consumed. Only 16 to 30% of the tetrabromide obtained could be induced to crystallize.

Anal. Calcd. for $C_5H_6Br_4$: Br, 82.45. Found: Br, 82.73.

Preparation of 1,4-Pentadiene, $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$.—One hundred twenty grams of purified crystalline 1,4-pentadiene tetrabromide was placed in a one-liter three-necked flask and covered with 450 cc. of alcohol. The flask was fitted with a mechanical stirrer and a reflux condenser. The top of the reflux was connected by a

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mide, prepared by the action of hydrochromic acid on allyl alcohol, contains a small amount of isopropyl bromide. H. Malbot [*Ann. chim. phys.*, [6] 19, 355 (1890)] has shown allyl iodide to be easily converted into isopropyl iodide by the action of hydriodic acid.

[21] Demjanow and Dojarenko, *Ber.*, 40, 2590 (1907).

[22] Tollens and Wagner, *ibid.*, 6, 589 (1873).

tube leading across and downward through a small coil condenser cooled by ice water into a train of two bottles immersed in a freezing mixture. The tetrabromide was dissolved in the alcohol by boiling. The temperature of the water in the reflux was maintained at 50°, which caused most of the alcohol to be returned but permitted the diolefin vapor to pass through into the receiver. Granular zinc (20-mesh) was then added to the reaction mixture in small portions. A vigorous reaction followed the addition of each portion and would soon have become too vigorous had not the addition been carefully controlled. This process was repeated until all but 2.5 g. of the theoretical 40.6 g. of zinc had been added. A large excess was then added and the reaction completed. About one-third of the alcohol was then distilled into the receiver.

The 130 cc. of liquid condensate was poured into twice its volume of cold water and the colorless, lighter, oily layer separated. The yield of crude diolefin was 9.35 g. or 44.5%. The product was dried and fractionated, yielding 6.2 g. of 1,4-pentadiene boiling at 29–30' (corr.); d^0_{25} 0.774.

Five grams of the purified 1,4-pentadiene was dissolved in chloroform and treated dropwise with a solution of bromine in chloroform to complete saturation. The chloroform was evaporated at room temperature and the crystalline product washed twice with cold alcohol and dried. The yield of crude solid was 8 g. or 28%. After two recrystallizations from hot alcohol, 5.2 g. of 1,4-pentadiene tetrabromide was obtained as pure white pearly leaves melting sharply at 86°.

Summary

A nuclear synthesis for a-olefins has been described. The synthesis consists in building up, by well-known reactions, the corresponding @-alkoxyalkyl bromide and the decomposition of this product, in alcoholic solution, by zinc dust. Nine β-bromo ethers of this type are described for the first time.

The method has been applied to the preparation of pentene-1, hexene-1, 4-methylpentene-1 and 5-methylhexene-1. The boiling points of the olefin so prepared agree closely with those given in the literature for the same products as prepared by other low-temperature methods. 1,4-Pentadiene has been prepared by a modification of the same procedure.

A tentative rule has been formulated stating the relationship between the boiling point of an a-olefin and the corresponding saturated hydrocarbon. The usual rule relating boiling points to branching chain structure has been more specifically stated in its application to olefins.

The application of the synthesis to the preparation of other olefins and diolefins is being continued.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF VIRGINIA, No. 63]

THE CONFIGURATIONS OF THE UNSATURATED DIBROMO 1,4-DIKETONES AND KETONIC ACIDS. SYNTHESIS AND STRUCTURE OF CIS AND TRANS BETA-BENZOYLDIBROMO-ACRYLIC ACIDS AND SOME OF THEIR DERIVATIVES.[1] STUDIES ON UNSATURATED 1,4-DIKETONES. V[2]

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This investigation was undertaken in order to establish conclusively the configurations of the unsaturated 1,4-ketonic acids, and if possible to establish inter-relationships between this series and the unsaturated 1,4-diketones, the configurations of which in many cases have already been determined with a considerable degree of certainty.

β-Benzoylacrylic acid has long been known[3] and has been widely studied,[4] but in spite of this its configuration has not been experimentally established up to this time. The acid is prepared from maleic anhydride, but it undoubtedly possesses a *trans* configuration[4j,k] as is now shown by the results of some recent studies which I will discuss in detail in the next paper of this series.[5] The hypothetical labile *(cis)* isomer remains as yet unknown despite many attempts to synthesize it.[4d,k] The yellow ester of the *trans* acid[4d,e,f,g,h] has been rearranged by the absorption of light energy into a labile colorless isomer which corresponds to the *cis* form, and the stability or energy relationship of these two isomeric esters is exactly analogous to that of other known *cis–trans* stereoisomeric pairs such as maleic and fumaric acids. Both the *cis* and *trans* esters, however, give the same yellow stable *(trans)* acid whenever hydrolysis is successful.

In view of these facts it seemed desirable to prepare the hitherto unknown *cis* and *trans* β-benzoyldibromo-acrylic acids and their esters, since

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[1] Presented at the meeting of the American Chemical Society at Atlanta, April 9, 1930.

[2] The preceding paper, Lutz, THIS JOURNAL, 51, 3008 (1929), entitled "1,6-Addition of Hydrogen to Unsaturated 1,4-Diketones," constitutes the fourth paper in this series.

[3] (a) H. v. Pechmann, *Ber.*, 15, 881 (1882); (b) Koenigs and Wagstaffe, *ibid.*, 26, 558 (1893); (c) Gabriel and Colman, *ibid.*, 32, 395 (1899); (d) Kozniewski and Marchlewski, *Bull. Acad. Sci. Cracow*, 81 (1906); (e) Bougault, *Ann. chim. phys.*, [8] 15, 296, 498 (1908).

[4] See also (a) Koenigs and Jaegle, *Ber.*, 28, 1048 (1895); (b) Bougault, *Comfit. rend.*, 146, 140 (1908); 147, 476 (1908); (c) Kohler and Engelbrecht, THIS JOURNAL, 41, 768 (1919); (d) Rice, *ibid.*, 45, 222 (1923); (e) 45, 232 (1923); (f) 48, 269 (1926); (g) 50, 229 (1928); (h) 50, 1481 (1928); (i) 52, 2094 (1930); (j) Bogert and Ritter, *Proc. Nat. Acad. Sci.*, 10, 363 *(1924)*; THIS JOURNAL, 46, 2871 (1924); (k) 47, 526 (1925); (1) Cattelain, *Bull. soc. chim.*, 41, 352 (1927).

[5] Lutz, THIS JOURNAL, 52, 3423 (1930).

in these compounds the ethylenic hydrogen atoms, which in all probability are largely responsible for the lability, are replaced by two bromine atoms.

In this research I have been able to synthesize *cis* and *trans* β-benzoyldibromo-acrylic acids and the corresponding esters from dibromo maleic and fumaric acids. The reduction of both acids to the same β-benzoylpropionic acid confirms the structures that have been assigned. Both acids are stable and are not affected by the reagents usually employed to bring about direct stereochemical rearrangement.

The stereochemical stability of these acids was not unexpected in view of the fact that dibromo maleic and fumaric acids do not readily rearrange,' one into the other, whereas the unsubstituted maleic and fumaric acids are mutually interconvertible, from *cis* to *trans* by the action of hydrochloric acid, halogens, etc., and from *trans* to *cis* by the absorption of light energy.[7] Of course *trans* isomers may be converted into *cis indirectly* despite unfavorable energy relations, and this sometimes with great ease; but these transformations usually involve, as the driving force, the formation of ring compounds, as is illustrated by the conversion of fumaric and dimethylfumaric acids[8] into the corresponding maleic *anhydrides,* and of dibromofumaryl chloride into dibromomaleil *pseudo* chloride.[6d] Transformations of this sort are not pertinent to this discussion since the energy relations referred to above concern only inversions of the configuration of the double bond without other change in the molecule. This other phase of the subject will be treated in later papers.

The effect of substitution for ethylenic hydrogen in unsaturated 1,4-diketones on the stereochemical stability of the *cis–trans* isomeric pairs, is of interest in this connection. The labile *cis* forms of the unsaturated 1,4-diketones in which the ethylene double bond remains unsubstituted, are in general prepared by the action of sunlight on the trans forms,[9] and they are easily rearranged into the stable *trans* isomers by the action of catalysts such as iodine, hydrochloric acid, etc.[9] However, when halogens[10] or a methoxyl[11] are substituted for hydrogen on the ethylene double bond, it is no longer possible to prepare the *cis* isomers directly in this way. Furthermore, the *cis* isomers, obtained indirectly,[10] are considerably more stable than those in which the ethylene double bond is unsubstituted. The labile dibromo derivative, to be sure, is rearranged into the *trans* form

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[6] Compare: (a) Wislicenus, *Ann.,* 246, 89 (1888); (b) Michael, *J. prakt. Chem.,* [2] 46,222 (1892); (c) 52,372 (1895); (d) Ott, *Ann.,* 392,267 (1912).

[7] Stoermer, Ber., 42,4870 (1909); etc.

[8] Wislicenus, *Ann.,* 246, 93 (1888); Volhard, *ibid.,* 268, 256 (1892); Tanatar, *ibid.,* 273, 31 (1893); Fittig and Kettner, ibid., 304, 165 (1898).

[9] (a) Paal and Schulze, *Ber.,* 35, 168 (1902); (b) Conant and Lutz, THIS JOURNAL, 45, 1303 (1923).

[10] Conant and Lutz, *ibid.,* 47, 881 (1925).

[11] Lutz, *ibid.,* 48, 2905 (1926).

by the action of iodine and sunlight,[10] but it is perfectly stable toward the action of aluminum chloride as has now been shown, whereas the unsubstituted cis dibenzoylethylene itself is largely rearranged into the *trans* isomer under the same conditions.[5] The *cis* methoxy compound[12] is quite stable.

The lability of the *cis* isomers is undoubtedly due in part at least to a lack of balance of forces within the molecule, which is accentuated when relatively light and mobile hydrogen atoms occupy two positions on the ethylene double bond opposite and also alpha to much larger groups of an unsaturated character such as benzoyl and carboxyl. The ethylenic hydrogens of benzoylacrylic acid, for instance, are labile, as is shown by the mechanism[4j,k] and ease of formation of "Pechmann dyes" in which enolization of alpha hydrogen destroys the *cis–trans* asymmetry of the ethylene double bond. The substitution of bromine probably alters the difference in energy content of the *cis* and *trans* forms but undoubtedly it also increases the stereochemical stability by sheer inactivation of the molecule, for it is well known that a highly substituted double bond is often very unreactive. The hypothetical *cis* benzoylacrylic acid undoubtedly possesses a high degree of lability, and if ever formed it always rearranges to the stable (*trans*) isomer under the experimental conditions involved in any synthesis. On the other hand, the elimination of mobile groups by the substitution of bromine for the ethylene hydrogens certainly increases the stereochemical stabilities to such an extent that both *cis* and *trans* isomers are easily obtained and defy rearrangement, even under the drastic conditions of a Friedel and Crafts reaction.

Cis **β-Benzoyldibromo-acrylic Acid and its *Derivatives.*** — *Cis* β-benzoyldibromo-acrylic acid (II) was prepared by the Friedel and Crafts reaction from dibromomaleic anhydride using benzene and aluminum chloride. The synthesis, structures and reactions are outlined in Diagram I. The *cis* acid, as will be shown, is not isomerized in the course of the Friedel and Crafts reaction as happens in the analogous preparation of β-benzoylacrylic acid from maleic anhydride,[3,4,5] and it is stable toward the reagents that are ordinarily effective in rearranging labile isomers. It is readily reduced by zinc and acetic acid to the known benzoylpropionic acid (VI), and it is esterified by the action of methyl alcohol saturated with dry hydrogen chloride. Hydrolysis of the ester with cold alcoholic sodium hydroxide produces the *cis* acid in good yield, but when aqueous sodium hydroxide is used the molecule undergoes cleavage, and a nearly theoretical yield of benzoic acid is obtained. In these experiments there was found no evidence of rearrangement of the sort that takes place under similar conditions in the hydrolysis of the unsubstituted labile esters of β-benzoylacrylic acid.[4d]

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[12] Both forms of dibenzoylmethoxyethylene are known, and both are stable, but the configurations have not as yet been established (see Ref. 11).

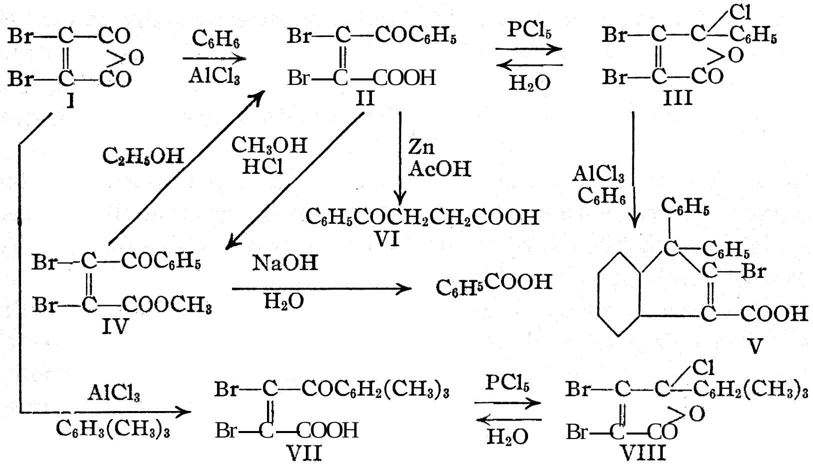


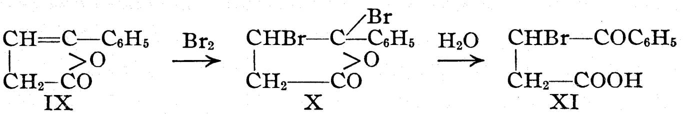
DIAGRAM I

A number of mesitoyl analogs of the compounds described above have been prepared and studied; the results are described in the experimental part, and are referred to also in Diagram I.

The β-benzoyldibromo-acrylic acid, prepared from dibromomaleic anhydride, has the *cis* configuration as is shown by the following facts. The ester of the isomeric *trans* acid has been prepared by a synthesis from dibromofumaric acid, which leaves no doubt as to its structure, and from this ester by hydrolysis is obtained the corresponding and isomeric *trans* acid. No inter-transformations between the two series have been observed, and the various configurations, therefore, must be stable, and must correspond to those of the starting materials. Furthermore, the acid chloride obtained from the *cis* acid behaves as if it were of the pseudo or chloro lactone type (111), in contrast to the normal behavior of the acid chloride obtained from the *trans* acid (XXI).

The acid chloride of *cis* benzoyldibromo-acrylic acid (III) is formed readily by the action of phosphorus pentachloride on the free acid and is a colorless solid melting at 82.5°. The possibility of rearrangement in the process is excluded since on hydrolysis with water the original acid is recovered unchanged. This hydrolysis, however, takes place extremely slowly as compared with the relative ease of hydrolysis of the *trans* acid chloride and acid chlorides in general (one week in contact with moisture was required for this hydrolysis). For this reason it may be separated from the by-product phosphorus oxychloride by shaking the crude mixture with water, a procedure which is without effect on the product but by which the phosphorus oxychloride is rapidly hydrolyzed. It dissolves in boiling methyl alcohol and crystallizes unchanged on cooling, and must therefore possess an inactive halogen atom since acid chlorides, the structures of which are known to be normal, react immediately with methyl alcohol to form esters, as actually does *trans* β-benzoyldibromo-acrylyl chloride. The pseudo or lactone structure (III) which I have assigned in Diagram I, and the cis relationship of carboxyl and carbonyl groups required on stereochemical grounds for this formulation, would therefore appear to be fully established. Further studies on this problem are being undertaken to confirm the above conclusion and to extend the work in a number of directions.

The pseudo or lactone forms of the acid chlorides of o-benzoylbenzoic acid[13] and ortho benzil mono and dicarboxylic acids[14] are known. The latter are characterized chemically by their inertness toward alcoholysis.[14] These compounds constitute excellent analogs of the pseudo acid chloride described above. No open-chain analog, so far as I know, has yet been made, but a closely related compound has been prepared by the addition of bromine to the internal anhydride of β-benzoylpropionic acid (IX).[15] The product is a substance which has the characteristics of a pseudo P-benzoyl-β-bromopropionyl bromide (X) since it hydrolyzes very slowly to β-benzoyl-β-bromopropionic acid (XI, see Diagram II). Diphthalyl, in the aromatic series, adds halogen similarly to give a di-pseudo acid chloride.[16]



$$\begin{array}{l}CH{=}C{-}C_6H_5\\ |\quad\ \ >O\\ CH_2{-}CO\end{array} \xrightarrow{Br_2} \begin{array}{l}\qquad\quad\ \ /Br\\ CHBr{-}C{-}C_6H_5\\ |\qquad\quad >O\\ CH_2{-}{-}CO\end{array} \xrightarrow{H_2O} \begin{array}{l}CHBr{-}COC_6H_5\\ |\\ CH_2{-}COOH\end{array}$$

IX X XI

DIAGRAM II

The Friedel and Crafts Reaction on Cis (ψ)-β-Benzoyldibromo-acrylyl Chloride.—Cis pseudo β-benzoyldibromo-acrylyl chloride was treated with aluminum chloride and benzene in a typical Friedel and Crafts reaction. It was hoped when the work was originally started that the acid chloride might react in part normally to give some cis dibenzoyldibromoethylene, for as is now shown this latter product is stable under the conditions of the experiment. No trace of such a product was isolated, however, nor was there obtained the expected unsymmetrical 4,4-diphenyl-1,2-dibromocrotolactone (XII) analogous to the similar products obtained from succinyl chloride,[17] meso dichlorosuccinyl chloride,[18] and phthalyl chloride.[19] This hypothetical lactone (XII) may be formed as an inter-

[13] (a) Haller and Guyot, *Bull. soc. chim.*, [3] 25, 54 (1901); (b) Meyer, *Monatsh.*, 25, 475, 1181 (1904); 28, 1235 (1907). See also (c) Martin, THIS JOURNAL, 38, 1142 (1916); (d) McMullen, *ibid.*, 38, 1228 (1916); (e) Hantzsch, *Ber.*, 52, 1572 (1919).

[14] Hantzsch and Schwiete, *ibid.*, 49, 213 (1916).

[15] Fittig and Ginsberg, *Ann.*, 299, 19 (1898).

[16] Ador, *ibid.*, 164, 246 (1872); see also Ref. 14.

[17] Auger, *Ann. chim. phys.*, [6] 22, 310 (1891); *Bull. soc. chim.*, [2] 49, 345 (1888).

[18] Lutz, THIS JOURNAL, 49, 1106 (1927).

[19] Baeyer, *Ann.*, 202, 50 (1880).

mediate product in the reaction, however, but the lactone ring opens with the introduction of a third phenyl group into the 4-position (see XIII), accompanied or followed by an internal condensation with the loss of hydrogen bromide between the alpha bromine and an ortho hydrogen of one phenyl group, to close an indene ring. The suggested mechanism of this reaction is outlined in Diagram III.

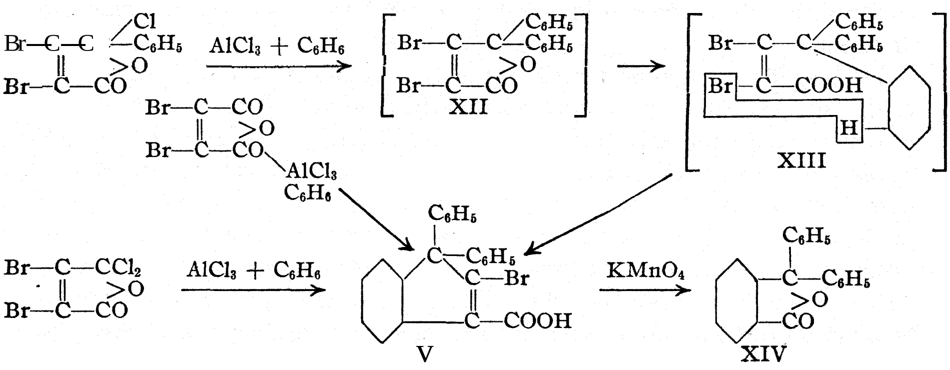


DIAGRAM III

It is interesting to note also in this connection that this same product can be obtained in small yields directly from dibromomaleic anhydride and from dibromomaleil chloride by the Friedel and Crafts reaction. In the former case possibly some of the cis β-benzoyldibromo-acrylic acid formed reacts further in the same general way that o-benzoylbenzoic acid reacts with aluminum chloride and benzene to give diphenylphthalide.[20] In the latter case dibromomaleil chloride reacts in the pseudo form as does phthalyl chloride.[19]

The structure of this new substance, 1,1-diphenyl-2-bromo-3-carboxyindene (V), is evident from analysis, properties and its oxidation product. It is an acid with one carboxyl group, forms salts readily, is dissolved by approximately one equivalent of sodium hydroxide, and loses carbon dioxide when heated above its melting point. On oxidation in alkaline solution with potassium permanganate it gives a good yield of diphenylphthalide (XIV), the structure of which is known.[19] The carbon skeleton of diphenylphthalide must therefore be present in the new compound, and it seems clearly established, at least, that three phenyl groups are attached to the 4-carbon and that one of them is attached to another position on the chain through loss of an ortho hydrogen and the alpha or beta bromine as hydrogen bromide. For obvious steric reasons the alpha bromine is undoubtedly the one which reacts since the formation of the five-membered indene ring would be the more likely result. The drastic oxidation of such a structure as is suggested would be expected to yield diphenylphthalide.

[20] H. v. Pechmann, *Ber.*, **14**, **1865** (1881).

If the above conclusions as regards structure and mechanism are correct, and if one assumes that the indene ring is a cis ring, then the stereochemical mode of closing the ring by the Friedel and Crafts reaction would appear to be trans, since the bromine atom is trans with respect to the phenyl group with which it reacts, and since rearrangement preceding reaction seems unlikely in view of the general stability of the cis dibromo compounds under these conditions. This idea is illustrated by Formula XIII in Diagram III. However, since the mechanism of this peculiar step in the reaction is not clear, little significance can be attached to this point.

That cis β-benzoyldibromo-acrylyl chloride has the pseudo structure is evident (though perhaps not conclusively proved) by its failure to react readily with methyl alcohol. It is clearly shown that there exists a cis relationship between the acid chloride and benzoyl radicals, whether the compound actually exists in the pseudo form or not, because the acid chloride undergoes the Friedel and Crafts reaction as if the pseudo form either did actually exist or was potentially available through a tautomerism possible only in a cis compound, and because the stereoisomeric acid chloride behaves in every way normally, as will be shown in the folowing section.

Trans β-Benzoyldibromo-acrylic Acid and **its** Derivatives.—All efforts to prepare the trans derivatives of β-benzoyldibromo-acrylic acid by rearranging the corresponding cis isomers have failed. The action of halogens and sunlight, of boiling concentrated hydrochloric acid, and of cold alcoholic sodium hydroxide, were without effect. The compounds of this series, then, despite the fact that they possess a cis configuration, are extremely stable.

The synthesis of trans β-benzoyldibromo-acrylic acid and its derivatives was accomplished through the use of dibromofumaric acid as the starting material. The reactions and structures are outlined in Diagrams IV **and** V.

Dibromofumaryl chloride reacts with aluminum chloride and benzene to give trans dibenzoyldibromo-ethylene (XVIII, known as the "high melting beta" stable isomer[10]). Dibromofumaric monomethyl ester monochloride (XX) was obtained from the above dichloride by partial alcoholysis of one acid chloride group by means of one equivalent of methyl alcohol. Subsequent condensation with benzene and aluminum chloride gave fair yields of β-benzoyldibromo-acrylic methyl ester (XXII), which was converted readily into the corresponding trans acid (XIX) by hydrolysis with cold alcoholic sodium hydroxide. Hydrolysis of the ester by means of aqueous sodium hydroxide, however, gave nearly theoretical yields of benzoic acid through cleavage of the molecule.

The relationships established between the various new derivatives of dibromofumaric acid confirm the structures and configurations assigned in Diagram (IV). The acid chloride (XVI) is easily hydrolyzed to the original acid, and may be alcoholized, partially to dibromofumaric monomethyl

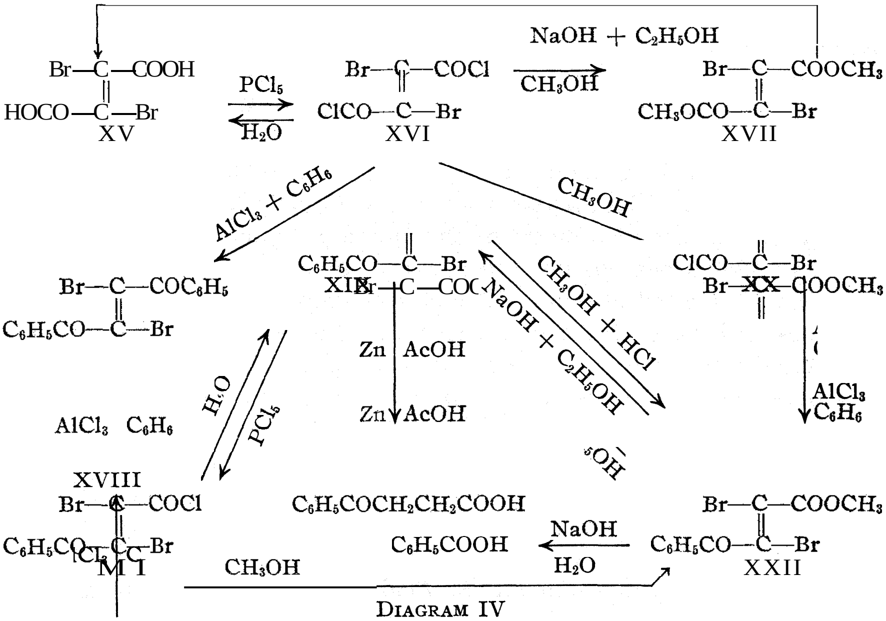


DIAGRAM IV

ester monochloride (XX), and completely to dimethyldibromofumarate (XVII). Dibromofumaric monomethyl ester monochloride has not as yet been isolated in a pure state free from dibromofumaryl chloride and dimethyl dibromofumarate. That it exists and has the character of a normal acid chloride is shown by the Friedel and Crafts reaction described above, and by the fact that an excess of methyl alcohol, acting on the original dichloride, gives the dimethyl ester. Furthermore, the analogous mono acid chloride monomethyl ester of fumaric acid has been isolated in a pure state and studied.[21,5] Dimethyl dibromofumarate is readily hydrolyzed by means of cold alcoholic sodium hydroxide and dibromofumaric acid is regenerated. Thus it is shown that the configurations have remained unchanged throughout these transformations, and that the new derivatives belong indeed to the *trans* series.

Trans β-benzoyldibromo-acrylic acid is easily esterified by saturating a methyl alcohol solution with dry hydrogen chloride. It is reduced readily by zinc and acetic acid to the known β-benzoylpropionic acid.[22] It is converted by the action of phosphorus pentachloride into an acid chloride which is of the normal type, as is shown by the ease with which it is hydrolyzed to the acid by water, and is alcoholized to the ester by methyl alcohol. The acid chloride reacts normally in the Friedel and Crafts reaction to give the known "high melting" *(trans)* dibenzoyldibromo-ethylene.[10]

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[21] Anschütz and Baeumges, Ann., 461,188 (1928).

[22] H. v. Pechmann, Ber., 15, 881 (1882).

The mesitoyl analogs of *trans* β-benzoyldibromo-acrylic acid, its ester and acid chloride, have been made (see Diagram V). This acid chloride (XXV), and also dibromofumaryl chloride, are readily converted by means of aluminum chloride and mesitylene into *trans* diinesitoyldibromo-ethylene (XXIV).

The *trans* configurations of the acids of this series derived from dibromofumaric acid, are clearly established by their synthesis alone, because there is no reason to suppose that rearrangement in the course of the reaction is possible, even under the drastic conditions of the Friedel and Crafts reaction and of hydrolysis (the isomers of opposite configuration are prepared by other methods from dibromomaleic anhydride, and are stable; and no inter-transformations between the two series have been observed). The above conclusion is strikingly confirmed by the normal character of the *trans* acid chloride as contrasted with the pseudo character of the *cis* isomer.

Synthesis and Configuration of Unsaturated Dibromo 1,4-Diketones.—In the course of the experiments described above, *trans* dibenzoyl-[10] and dimesitoyldibromo-ethylenes have been synthesized, respectively, from *trans* benzoyl- and mesitoyl-dibromo-acrylyl chlorides and also from dibromofumaryl chloride, by the Friedel and Crafts reaction. The structure of *trans* dimesitoyldibromo-ethylene was shown by reducing it with zinc and acetic acid to the known dimesitoylethane (XXVII).[23]

The configuration of dibenzoyldibromo-ethylene is evidently *trans* since it is the stable isomer, as has already been shown[10] by the rearrangement of the *cis* isomer. The *trans* configuration is now confirmed by the above syntheses, as is evident from the following considerations. Both of the starting materials are known to have the *trans* configuration and are stable. There is no reason to suppose that inversion could occur at any point in the syntheses because the double bond is inactive and does not appear to enter into the reaction in any way, and because no group attached directly to the double bond undergoes replacement. The only conceivable way for rearrangement to occur would be through the change from a labile intermediate to a'stable isomer by the catalytic action of the reagents involved, as undoubtedly happens[5] in the preparation of the stable *(trans)* benzoylacrylic acid from maleic anhydride. The labile dibenzoylethylene (unsubstituted) is actually rearranged[5] under the conditions involved in the Friedel and Crafts synthesis. If such a rearrangement were to occur in the reaction in question, it would mean that the final stable product (actually obtained exclusively) would have the *cis* configuration (opposite that of the starting materials), and that the intermediate labile isomer necessarily assumed, would be *trans*, a relationship which is highly improbable since it is opposite that of maleic and fumaric acids and of cis and *trans* dibenzoylethylenes. In the reaction in question the labile dibromo isomer

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[23] Conant and Lutz, THIS JOURNAL, **45**, 1303 **(1923).**

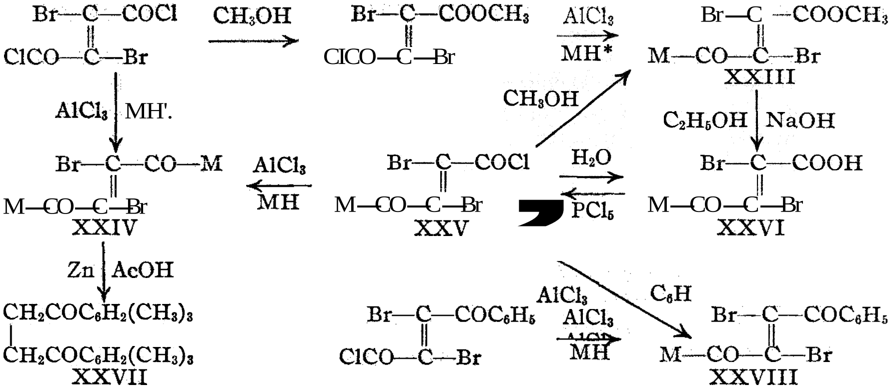
is not formed in the reaction as an intermediate product because (contrary to the analogous unsubstituted labile dibenzoylethylene) it is perfectly stable under the conditions of the experiment, as is now shown, and it would have been isolated among the reaction products if it had been formed in significant amounts. Therefore, the stable isomer only is produced in the reaction, and it must correspond in configuration to dibromofumaric acid and *trans* benzoyldibromo-acrylic acid from which it was synthesized.

The above statement concerning the stability of the known labile *(cis)* dibenzoyldibromo-ethylene under the conditions of the Friedel and Crafts reaction is based on the complete recovery of a sample of the labile isomer after it was subjected to the action of the reagents in a typical experiment. The colorless *cis* dibenzoyldibromo-ethylene reacts immediately with aluminum chloride in benzene to give the same sort of highly colored complex product as that obtained in the Friedel and Crafts reaction itself on dibromofumaryl chloride and on *trans* benzoyldibromo-acrylyl chloride; but on hydrolysis the *cis* product may be recovered unchanged. Furthermore, when dibromofumaryl chloride is added to a mixture of *cis* dibenzoyldibromo-ethylene, aluminum chloride and benzene, the normal Friedel and Crafts reaction takes place with the formation of the usual yield of *trans* dibenzoyldibromo-ethylene, and the bulk of the *cis* isomer introduced at the start can be recovered. Qualitatively the properties of these complex halochromic compounds correspond exactly in every way. The complex compound from the *cis* isomer apparently does not involve the ethylene double bond (at least as regards the major valence forces), since otherwise the asymmetry of the double bond would be destroyed and the stable form produced, a point of some significance, perhaps, in connection with theories of halochromism. It seems reasonably certain, then, that the conditions in these tests are nearly enough identical with those existing in actual experiment to justify the conclusion that *cis* dibenzoyldibromo-ethylene is stable under the conditions involved in the Friedel and Crafts reaction.

As a consequence of the relationships discussed above the configurations of the *cis* ("low-melting alpha") and *trans* ("high-melting beta") isomers of dibenzoyldibromo-ethylene (and by analogy those of the corresponding dichloro compounds) are established. Furthermore, since the stability relationship between these *cis–trans* isomeric pairs corresponds to that between maleic and fumaric acids, the validity of conclusions regarding the configurations of various other symmetrical unsaturated 1,4-diketones based on exactly analogous stability or energy relationships and upon the synthesis from fumaryl chloride, is confirmed.

It now becomes possible to prepare unsymmetrical unsaturated dibromo 1,4-diketones. The synthesis of a typical derivative is outlined in Diagram V. *Trans* benzoyldibromo-acrylyl chloride reacts with aluminum chloride and mesitylene to give *trans* benzoylmesitoyldibromo-ethylene (XXVIII);

the same product is obtained from *trans* mesitoyldibromo-acrylyl chloride (XXV) by the action of benzene and aluminum chloride.



* M = Mesityl, —$C_6H_2(CH_3)_3$. MH = Mesitylene, $C_6H_3(CH_3)_3$.

DIAGRAM V

Several points of interest arise in connection with this synthesis. First, the melting point of dibenzoyldibromo-ethylene is 213°, but when one mesityl group is substituted for phenyl, the melting point drops to 102.5°, then rises again to 198.5° upon substitution of the second mesityl group.

A second point of interest concerns the use of benzene in place of carbon disulfide as the solvent in the Friedel and Crafts reaction utilizing a more active aromatic hydrocarbon such as, for example, mesitylene. In the reaction between fumaryl chloride, mesitylene and aluminum chloride, with benzene as the solvent, mesitylene reacts exclusively.[5] Curiously enough, benzene reacts exclusively under similar conditions when dibromofumaryl chloride or *trans* benzoyl- or mesitoyl-dibromo-acrylyl chlorides are used in place of fumaryl chloride.

Conclusion

The evidence for the configurations assigned the two stereoisomeric benzoyldibromo-acrylic acids and their derivatives may be briefly summarized as follows. In every preparation of a compound in either the *cis* or *trans* series, there is formed exclusively one of the two possible stereoisomers and in no case has stereochemical rearrangement been observed. The configurations, therefore, correspond, respectively, to those of the two starting materials, dibromo maleic and fumaric acids, and are confirmed by the fact that the acid chlorides of the series derived from dibromomaleic acid are of the pseudo type, whereas those derived from dibromofumaric acid are normal in character.

The configurations of the unsaturated dibromo 1,4-diketones are established by the synthesis of the *trans* forms from compounds of known configurations under conditions which preclude the possibility of rearrangement.

Experimental Part

Dibromomaleic acid was prepared by the bromine oxidation of furoic acid to mucobromic acid[24] followed by further oxidation with fuming nitric acid.[25] The anhydride (I) was prepared by passing a stream of dry carbon dioxide over the molten acid at 130–140°. In an alternative method 80 g. of dibromomaleic acid was refluxed with an excess of thionyl chloride. After distilling the excess of reagent, 70 g. of sufficiently pure anhydride was obtained. An attempt was made to prepare the acid chloride by treating dibromomaleic acid with phosphorus pentachloride, but there was obtained only dibromomaleic anhydride, which resisted further action of the reagents.

Dibromofumaric acid (XV)[26,6d] was prepared by the action of bromine vapor on a concentrated aqueous solution of acetylene dicarbonic acid, and was isolated by evaporating the solvent in vacuum desiccators and filtering off successive crops of crystals. The low-melting end fractions containing dibromomaleic acid were discarded. The acid chloride[6d] (XVI) was prepared by the action of phosphorus pentachloride.

Dibromofumaric Monomethyl Ester Monochloride (XX), $CH_3OCOCBr{=}CBrCOCl$.—Dibromofumaryl chloride was partially alcoholized with one equivalent of methyl alcohol in carbon disulfide or benzene as the solvent. The mixture was allowed to stand for five to six hours and was refluxed for a short time. When used in a reaction the product was not isolated. In one experiment the product was subjected to a series of fractional distillations under diminished pressure using a Vigreux column, but a pure sample was not obtained. Small amounts of maleic anhydride were isolated, formed possibly by decomposition and rearrangement. The unchanged dichloride present in considerable amounts was rearranged nearly completely by the long continued heating involved (80–120° at 7 mm. pressure), as was shown by the fact that dibromomaleic acid was obtained in considerable amounts on hydrolysis of some of the fractions (compare Ref. 6d). The best sample isolated was a nearly colorless oil; boiling point 83–86° at 3.5 mm. pressure.

Anal. Calcd. for $C_5H_3O_3Br_2Cl$: C, 19.59; H, 1.24; Br_2Cl, 63.77. Found: C, 20.93; H, 1.13; Br_2Cl, 64.67.

Dimethyl Dibromofumarate (XVII), $CH_3OCOCBr{=}CBrCOOCH_3$.—Dibromofumaryl chloride (15 g.) dissolved in methyl alcohol with the evolution of heat. The solution was decomposed in ice and sodium carbonate and was extracted with chloroform. The solution thus obtained was fractionally distilled under diminished pressure using a Vigreux column; 13.5 g. of colorless oil was obtained which finally solidified on cooling; yield 93%; colorless needles; melting point 41.5° (corr.) after several crystallizations from petroleum ether; boiling point 113–114° (corr.) at 5 mm.

Anal. Calcd. for $C_6H_6O_4Br_2$: C, 23.86; H, 2.00; Br, 52.93. Found: C, 23.95; H, 1.70; Br, 53.40, 53.44, 53.34.

Dimethyl dibromofumarate (0.5 g.) was dissolved in a solution of 0.15 g. of sodium in 10 cc. of alcohol and 1 cc. of water. After standing for eighteen hours, the solution was diluted with water, extracted with ether, acidified and again extracted with ether. This latter ether extract, on evaporation and vacuum desiccation, gave 0.4 g. of dibromofumaric acid.

Cis β-Benzoyldibromo-acrylic Acid (11), $C_6H_5COCBr{=}CBrCOOH$.—A mixture of 150 g. of dibromomaleic anhydride, 120 g. of finely ground aluminum chloride[27] and

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[24] Jackson and Hill, Ber., 11, 1671 (1878).

[25] Salmony and Simonis, *ibid.*, **38,** 2584 (1905).

[26] Lossen and Treibich, *Ann.*, 384, 324 (1911).

[27] In this and in all similar experiments a high grade of finely ground anhydrous aluminum chloride was used.

300 cc. of benzene was warmed gently for thirty minutes with mechanical stirring, and was then heated on a boiling water-bath for fifteen minutes. The dark colored pasty mass was decomposed in ice and hydrochloric acid, and the benzene layer separated and allowed to evaporate. The residue was crystallized from carbon tetrachloride; the yield of crude product melting at 78° was 124 g. (63%). A small amount of unchanged dibromomaleic anhydride was recovered from the filtrates.

The compound forms colorless crystals, melting point 92° (corr.) after repeated crystallizations from carbon tetrachloride; soluble in alcohol, ether, acetone; insoluble in ligroin: crystallizes from chloroform, and crystallizes from benzene and ethylene dibromide with solvent of crystallization.

Anal. Calcd. for $C_{10}H_6O_3Br_2$: Br, 47.87. Found: Br, 47.87.

When the above reaction mixture was heated for a greater length of time a small amount of colorless solid (m. p. 237.5–238°) was filtered from the benzene layer and was identified by a mixed melting point as 1,1-diphenyl-2-bromo-3-carboxyindene.

Samples of cis benzoyldibromo-acrylic acid in various solvents were subjected to the action of iodine or bromine and sunlight. Another sample was boiled with hydrochloric acid (20%) for several hours. In every case the acid was recovered unchanged.

Cis benzoyldibromo-acrylic acid (1 g.) was reduced with 2 g. of zinc dust and acetic acid. Considerable heat was evolved. The product was isolated by filtering, diluting with water, extracting with ether, evaporating and crystallizing the residue from water. A yield of 0.4 g. (80%) of β-benzoylpropionic acid melting at 114–115° was obtained and identified by a mixed melting point.

Cis-8-[2,4,6-trimethylbenzoyl]dibromo-acrylic Acid (XXVI), $(CH_3)_3C_6H_2COCBr{=}CBrCOOH$.—A mixture of 40 g. of dibromomaleic anhydride, 22 g. of mesitylene, 80 cc. of carbon disulfide, and 48 g. of aluminum chloride was refluxed for twenty minutes with efficient mechanical stirring. The red mass was decomposed in ice and hydrochloric acid. The carbon disulfide layer was separated and on cooling deposited 46.5 g. of nearly pure product melting at 153–154°; yield, 79%.

It forms pale yellowish rhombic crystals; melting point 157° (corr.) after three crystallizations from benzene: soluble in acetone, alcohol, ether, ethyl acetate and acetic acid; insoluble in cold chloroform and hot ligroin.

Anal. Calcd. for $C_{13}H_{12}O_3Br_2$: C, 41.52; H, 3.22; Br, 42.50. Found: C, 41.74; H, 3.23; Br, 42.43, 42.72.

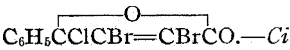
Cis **β-Benzoyldibromo-acrylic** Methyl Ester (IV), $C_6H_5COCBr{=}CBrCOOCH_3$.—A solution of 25 g. of cis β-benzoyldibromo-acrylic acid in 40 cc. of methyl alcohol was saturated with dry hydrogen chloride and allowed to stand overnight. The solution was decomposed in ice and sodium carbonate, extracted with ether, dried with anhydrous potassium carbonate and distilled under diminished pressure. The crude ester boiled at 162–164° under 3.5 mm. pressure and solidified on cooling; yield, 19 g (73%).

It gives colorless crystals; melting point 71.5° (corr.) after several crystallizations by dissolving in ethyl bromide, diluting with a little petroleum ether, seeding and allowing the solution to stand.

Anal. Calcd. for $C_{11}H_8O_3Br_2$: C, 38.04; H, 2.32. Found: C, 38.22; H, 2.37.

Hydrolysis.—The ester was allowed to stand overnight in a solution of a small excess of one equivalent of sodium in 95% ethyl alcohol. On diluting with water. acidifying, extracting with ether and crystallizing the product from carbon tetrachloride a sample of the cis acid was obtained and identified.

Cis **β-(ψ)-Benzoyldibromo-acrylyl** Chloride (111),



$C_6H_5\overset{\ulcorner\!\!-\!\!-\!\!-O-\!\!-\!\!-\urcorner}{CClCBr{=}CBrCO}$.—*Cis* β-benzoyldibromo-acrylic acid (15 g.) was treated with 9 g. of phosphorus pentachloride.

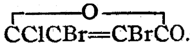
The liquid product was diluted with petroleum ether, cooled and stirred until the acid chloride crystallized; yield, 12 g. (76%).

It forms colorless crystals; melting point 82.5° (corr.) after several crystallizations from chloroform and petroleum ether mixtures; soluble in chloroform and benzene; insoluble in ligroin; crystallizes unchanged from methyl alcohol, but gives an oil on long continued boiling.

Anal. Calcd. for $C_{10}H_5O_2Br_2Cl$: Cl, Br, 55.26. Found: 55.00.

A sample of the acid chloride was very slowly hydrolyzed upon standing in a moist condition for one week. The regenerated acid was isolated and identified.

In one experiment the crude acid chloride was shaken with water to remove the phosphorus oxychloride by hydrolysis. In a short time the acid chloride crystallized, was filtered, dried, recrystallized and identified.

Cis **β-(ψ)-[2,4,6-trimethylbenzoyl]dibromo-acrylyl** Chloride (XXV), $(CH_3)_3C_6H_2$-  $\overbrace{CClCBr{=}CBrCO}^{O}$.—*Cis* β-mesitoyldibromo-acrylic acid (7.5 g.) was treated with 4.2 g. of phosphorus pentachloride. The mixture liquefied with the evolution of hydrogen chloride. On diluting with petroleum ether, cooling and subsequently evaporating, several crops of crystals were obtained; yield, 6.7 g. (85%).

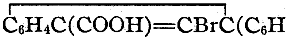
It forms long colorless needles; melting point 76° (corr.) after three crystallizations from ligroin; soluble in hot methyl alcohol and crystallizes unchanged on cooling; soluble in hot ligroin, and in cold chloroform, acetone, benzene, ethyl acetate and acetic acid.

Anal. Calcd. for $C_{13}H_{11}O_2Br_2Cl$: C, 39.63; H, 2.81; Br, Cl, 49.52. Found: C, 39.76, 40.09, 39.63; H, 3.09, 3.10, 2.63; Br, Cl, 49.20.

Hydrolysis was accomplished by heating a sample of the acid chloride with water for five hours. The crude acid thus obtained was recrystallized from benzene and identified.

The above acid chloride was treated in several experiments with mesitylene, carbon disulfide and aluminum chloride, but only scarlet resinous products were obtained from which in a few cases small amounts of a colorless solid were isolated; melting point 240–242° after recrystallizing from alcohol; insoluble in chloroform and benzene; soluble in sodium carbonate and precipitated by acids.

Anal. Calcd. for $C_{21}H_{22}BrO_3$: C, 62.68; H, 5.51; Br, 19.87. Found: C, 63.01, 63.06; H, 5.56, 5.48; Br, 20.12, 20.36.

1,1-Diphenyl-2-bromo-3-carboxyindene (V),  $\overline{C_6H_4C(COOH){=}CBrC}(C_6H_5)_2$.—*Cis* (ψ)-benzoyldibromo-acrylyl chloride was treated with 50 cc. of benzene and 10 g. of aluminum chloride, and the mixture was stirred until it became a red pasty mass. Benzene (50 cc.) was added and the mixture was stirred and heated on a water-bath for fifteen minutes. After decomposing in ice the product was precipitated from the benzene layer by diluting with petroleum ether; yield, 9 g. (71%).

It gives colorless microscopic prisms; melting point (decomp.) 242–243° (corr.) after three crystallizations from benzene; when heated above its melting point carbon dioxide was evolved and was detected qualitatively; soluble in cold acetone, and hot alcohol and chloroform; insoluble in ligroin.

Anal. Calcd. for $C_{22}H_{15}O_2Br$: C, 67.53; H, 3.84; Br, 23.73. Found: C, 67.66; 67.50; H, 3.87, 3.99; Br, 25.71.

In a qualitative experiment a sample of dibromomaleil chloride was prepared by heating dibromofumaryl chloride with an excess of aluminum chloride at 100" for three hours.[6d] The crude mixture was treated directly (without isolating the acid chloride) with benzene and refluxed for half an hour. On decomposition in ice, a large amount of resinous amorphous product was obtained from which a small yield of 1,1-diphenyl-2-bromo-3-carboxyindene was isolated and identified.

A sample of the acid dissolved in one equivalent of dilute sodium hydroxide. The sodium salt crystallized as shining leaflets upon the addition of an excess of sodium ion. When dissolved in water, the sodium salt gave precipitates with salts of silver, copper, calcium, barium, lead and magnesium. The acid is stable in boiling sodium hydroxide solution.

Oxidation.—A solution of 6 g. of 1,1-diphenyl-2-bromo-3-carboxyindene, 3 g. of sodium hydroxide and 7.5 g. of potassium permanganate (a slight excess of the calculated amount) was boiled for a short time. The purple color persisted. In another run, using slightly less than the calculated amount of permanganate, the color was quickly discharged. The mixture was decomposed with hydrochloric acid and sulfur dioxide, and gave 3.75 g. (85%) of nearly pure diphenylphthalide, which was identified by analysis and by a mixed melting point with a known sample prepared from phthalyl chloride by the Friedel and Crafts reaction.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 84.04, 83.69; H, 5.14, 5.06.

Trans **β-Benzoyldibromo-acrylic** Methyl Ester (XXII), $C_6H_5COCBr{=}CBrCOOCH_3$.—Methyl alcohol (10.5 g.) in 300 cc. of benzene was added over a period of two hours to 93 g. of well-stirred dibromofumaryl chloride. The mixture after standing for two hours was refluxed for five minutes Aluminum chloride (120 g.) was then added in small portions to the effectively stirred mixture. Color appeared only after about one-third of the aluminum chloride had been added; hydrogen chloride ceased to be evolved after the addition of the last portion. The brown mass was stirred for ten minutes and was decomposed in ice and hydrochloric acid. The benzene layer was cooled and 15 g. of the very insoluble dibenzoyldibromo-ethylene melting at 203–206° was filtered off and identified. The benzene solution was fractionally distilled under diminished pressure. The fraction boiling at 110° under 3 mm. pressure rapidly solidified in the side arm and receiver and was identified as dimethyl dibromofumarate; yield, 8 g. An intermediate fraction (6 g.) was collected, and then 52 g. of *fans* benzoyldibromo-acrylic acid methyl ester distilled at 170–180° under 3 mm. pressure and solidified on cooling.

It forms colorless prisms; melting point 80.5" (corr.) after four crystallizations from a mixture of ligroin and ethyl bromide; soluble in acetone, chloroform, benzene, ether, ethyl acetate and acetic acid; crystallizes from alcohol in thin scales.

Anal. Calcd. for $C_{11}H_8O_3Br_2$: C, 38.04; H, 2.32; Br, 45.94. Found: C, 37.96; H, 2.32; Br, 45.93, 46.31, 45.78.

A sample of the ester was suspended in boiling 20% hydrochloric acid for several hours and was recovered unchanged. It was sensitive to boiling aqueous alkaline solutions, sodium carbonate yielding dark colored solutions, and sodium hydroxide cleaving the molecule to give a nearly theoretical yield of benzoic acid and a low-melting acid containing halogen which has not yet been investigated.

Trans **β-Benzoyldibromo-acrylic** Acid (XIX), $C_6H_5COCBr{=}CBrCOOH$.—*Trans* benzoyldibromo-acrylic methyl ester (30 g.) was dissolved in a solution of 3 g. of sodium in 300 cc. of ethyl alcohol and 15 cc. of water, and the mixture was allowed to stand overnight. The solution was then diluted with water, extracted with ether and acidified. A second extraction with ether removed the organic acid which was liberated. The product was isolated by evaporating the ether solution and inducing the oily residue to crystallize; yield 20 g. (70%).

It forms colorless prisms; melting point 108° (corr.) after four crystallizations from chloroform by adding ligroin and seeding; soluble in acetone, alcohol, ether, benzene, ethyl acetate and acetic acid.

Anal. Calcd. for $C_{10}H_6O_3Br_2$: C, 35.95; H, 1.81; Br, 47.87. Found: C, 35.91; H, 1.92; Br, 47.81.

Reduction in the usual way by means of zinc and acetic acid gave a good yield of β-benzoylpropionic acid. The acid was partially converted to the methyl ester on standing in methyl alcohol saturated with dry hydrogen chloride.

Trans β-**Benzoyldibromo-acrylyl** Chloride **(XXI)**, $C_6H_5COCBr{=}CBrCOCl$.—Trans benzoyldibromo-acrylic acid (3.3 g.) reacted with 2.2 g. of phosphorus pentachloride to give a liquid product which was fractionally distilled under diminished pressure. The acid chloride distilled at 164° at 7 mm. pressure and solidified in the receiver; yield 2.5 g. (72%).

It forms colorless prisms; melting point 37° (corr.) after two crystallizations from petroleum ether; very soluble in chloroform and benzene.

Anal. Calcd. for $C_{10}H_5O_2Br_2Cl$: C, 34.02; H, 1.43; Br, Cl, 55.26. Found: C, 34.09; H, 1.70; Br, Cl, 55.50.

Hydrolysis by shaking a sample of the acid chloride with water gave a nearly quantitative yield of benzoyldibromo-acrylic acid.

Alcoholysis with methyl alcohol took place with the evolution of heat and with the formation of benzoyldibromo-acrylic methyl ester which was isolated and identified by a mixed melting point.

Trans **β-[2,4,6-Trimethylbenzoyl]dibromo-acrylic** Methyl Ester (XXIII), $(CH_3)_3$-$C_6H_2COCBr{=}CBrCOOCH_3$.—A mixture of 6.5 g. of methyl alcohol, 25 g. of mesitylene and 160 cc. of carbon disulfide was allowed to run into 56 g. of well stirred dibromofumaryl chloride over a period of half an hour. The mixture, after standing for four hours was refluxed for a few minutes; seventy-five grams of aluminum chloride was then added in small portions. The mixture was finally decomposed in ice and hydrochloric acid. The carbon disulfide solution was successively cooled, evaporated and diluted with petroleum ether. Two crystalline products were isolated: 5.6 g. of the difficultly soluble trans dimesitoyldibromo-ethylene, and 25 g. of the more soluble trans mesitoyldibromo-acrylic methyl ester; yield, 36%.

It gives pale yellow, short, thick prisms; melting point 115.5–116° (corr.) after three crystallizations from benzene by the addition of petroleum ether, and one crystallization from ligroin; soluble in acetone, ether, ethyl acetate, acetic acid and hot alcohol.

Anal. Calcd. for $C_{14}H_{14}O_3Br_2$: C, 38.04; H, 2.32; Br, 40.97. Found: C, 37.99; H, 2.45; Br, 40.86, 41.05.

Trans β-**[2,4,6-Trimethylbenzoyl]dibromo-acrylic** Acid **(XXVI)**, $(CH_3)_3C_6H_2CO$-$CBr{=}CBrCOOH$.—*Trans* mesitoyldibromo-acrylic methyl ester was hydrolyzed with cold alcoholic sodium hydroxide; 9.5 g. of the ester gave 2.5 g. of nearly pure acid; yield, 27%; pale yellow crystals; melting point 139° (corr.) after crystallizing twice from benzene and ligroin, and once from benzene; soluble in chloroform, acetone, ether, ethyl acetate, acetic acid and alcohol.

Anal. Calcd. for $C_{13}H_{12}O_3Br_2$: C, 41.52; H, 3.22; Br, 42.50. Found: C, 41.65, 41.69; H, 3.05, 3.61; Br, 42.25.

Trans β-**(2,4,6-Trimethylbenzoyl)dibromo-acrylyl** Chloride (XXV), $(CH_3)_3C_6H_2$-$COCBr{=}CBrCOCl$.—*Trans* β-mesitoyldibromo-acrylic acid (1.05 *g.)* reacted with 0.65 g. of phosphorus pentachloride to give an oil. On adding petroleum ether 0.6 g of the acid chloride crystallized; yield, 60%; very pale yellow crystals; melting point 73–73.5° (corr.) after several crystallizations from ligroin.

Anal. Calcd. for $C_{13}H_{11}O_2Br_2Cl$: BrCl, 49.52. Found: 50.06.

A sample of the acid chloride, when allowed to stand in water, was hydrolyzed to the acid.

When treated in the usual way with aluminum chloride, mesitylene and carbon disulfide, a good yield of *trans* dimesitoyldibromo-ethylene was obtained and identified by a mixed melting point.

A sample of the acid chloride was warmed with a little methyl alcohol. On cooling a crystalline product melting at 113° was isolated and identified by a mixed melting point as *trans* mesitoyl bromo-acrylic methyl ester.

Trans **Dibenzoyldibromo-ethylene (XVIII)**.—*Trans* benzoyldibromo-acrylic acid (0.33 g.) was treated with one equivalent of phosphorus pentachloride and the product, without removing the phosphorus oxychloride formed, was treated directly with 5 cc. of benzene and 1.5 g. of aluminum chloride. The reaction mixture was heated to boiling and when the evolution of hydrogen chloride subsided it was decomposed in ice. The benzene layer, on cooling, deposited 2.5 g. of pure *trans* dibenzoyldibromo-ethylene; yield, 64%.

In a second experiment 10 g. of dibromofumaryl chloride was added to a well-stirred mixture of 50 cc, of benzene and 12 g. of aluminum chloride. The product was isolated as above. The yield of pure *trans* dibenzoyldibromo-ethylene was 10 5 g. (85%).

In a third experiment one equivalent of bromine was added to a boiling chloroform solution of dibenzoylacetylene. The yield of *trans* dibenzoyldibromo-ethylene was raised to about 60%, nearly twice that previously obtained[10] when the mixture was cooled. The *cis* isomer in this case was isolated in a relatively small yield.

Cis **Dibenzoyldibromo-ethylene.**[10]—A sample of *cis* dibenzoyldibromo-ethylene (1 g.) was treated with benzene and aluminum chloride. A red-brown mass was obtained. The mixture was heated to boiling, and was allowed to stand for one minute. The deep red mixture was decomposed in ice and the product isolated by extracting with ether and evaporating the solvent; 0.9 g. of nearly pure *cis* dibenzoyldibromo-ethylene melting at 102–104° was recovered and identified by a mixed melting point. No traces of the *trans* isomer were isolated.

In another experiment 0.5 g. of *cis* dibenzoyldibromo-ethylene in 10 cc. of benzene and 1 g. of dibromofumaryl chloride was treated with 4 g. of aluminum chloride. The red pasty mixture was heated for several minutes and was then decomposed in ice. On cooling and diluting the benzene layer with petroleum ether 0.95 g. of *trans* dibenzoyldibromo-ethylene was obtained. On evaporating the filtrate an oil was obtained which crystallized when taken up in alcohol to give 0.4 g. of unchanged *cis* dibenzoyldibromo-ethylene.

Trans **Di-(2,4,6-trimethylbenzoyl)dibromo-ethylene (XXIV)**, $(CH_3)_3C_6H_2COCBr{=}CBrCOC_6H_2(CH_3)_3$.—Dibromofumaryl chloride (10 g.) was added slowly to a well-stirred mixture of 16 g. of aluminum chloride, 10 g. of mesitylene and 25 cc. of carbon disulfide. The product was decomposed in ice. The carbon disulfide layer, on cooling, deposited 7.5 g. of nearly pure product; yield, 49%; very pale yellowish crystals; melting point 198.5" (corr.) after four crystallizations from benzene; difficultly soluble in hot alcohol.

Anal. Calcd. for $C_{22}H_{22}O_2Br_2$: C, 55.25; H, 4.64; Br, 33.44. Found: C, 55.24; H, 4.64; Br, **33.53.**

When benzene was used in place of carbon disulfide in the above experiment only the corresponding dibenzoyldibromo-ethylene was obtained as the product.

A sample (1 g.) reacted with zinc dust and acetic acid with the evolution of considerable heat. From the filtrate 0.57 g. of nearly pure dimesitoylethane melting at 135–136.5° was isolated and identified by a mixed melting point; yield, 95%.

Trans **1-Benzoyl-2-[2,4,6-trimethylbenzoyl]dibromo-ethylene (XXVIII),** $C_6H_5CO-CBr{=}CBrCOC_6H_2(CH_3)_3$.—Benzoyldibromo-acrylic acid (1 g.) was treated with 0.67 g. of phosphorus pentachloride and the crude acid chloride was treated directly with carbon disulfide, 1 cc. of mesitylene and 2 g. of aluminum chloride. The red-brown mass was decomposed with ice, and the carbon disulfide layer was steam distilled. The oily residue was dissolved in methyl alcohol and on seeding deposited 0.15 g. of product; very pale yellowish crystals; melting point 102.5° (corr.) after two crystallizations from methyl alcohol, in which the substance dissolves when hot to give a yellow solution.

Anal. Calcd. for $C_{19}H_{16}O_2Br_2$: C, 52.30; H, 3.70. Found: C, 52.94; H, 3.86.

In a second experiment benzene was used as the solvent in place of carbon disulfide, but benzene reacted instead of mesitylene to give a good yield of *trans* dibenzoyldibromo-ethylene.

In a third experiment in which 0.1 g. of *trans* mesitoyldibromo-acrylyl chloride was treated with 1 cc. of benzene, 0.1 cc. of mesitylene and 0.6 g. of aluminum chloride, a yield of 0.06 g. of *trans* benzoylmesitoyldibromo-ethylene was isolated and identified by a mixed melting point.

Summary

Cis β-Benzoyldibromo-acrylic acid and a number of derivatives have been synthesized from dibromomaleic anhydride. The acid chloride is of the pseudo type and undergoes the Friedel and Crafts reaction to give 1,1-diphenyl-2-bromo-3-carboxyindene. The structure and mechanism of formation of the latter are discussed.

Trans β-Benzoyldibromo-acrylic acid and a number of derivatives have been synthesized from dibromofumaric acid. Incidental to the syntheses some new derivatives of dibromofumaric acid are described.

The unsaturated dibromo 1,4-diketones are prepared by the Friedel and Crafts reaction on the *trans* aroyl dibromo-acrylyl chlorides and on dibromofumaryl chloride. A method of preparing unsymmetrical, unsaturated dibromo 1,4-diketones is described.

The configurations of the unsaturated 1,4-diketones and ketonic acids are discussed.

UNIVERSITY. VIRGINIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF VIRGINIA, No. 64]

THE SYNTHESIS AND CONFIGURATIONS OF UNSATURATED 194-DIKETONES AND KETONIC ACIDS, AND THE STEREOCHEMICAL MECHANISM OF THE ADDITION OF BROMINE. STUDIES ON UNSATURATED 1,4-DIKETONES. VI

BY ROBERT E. LUTZ

RECEIVED MAY 21, 1930 PUBLISHED AUGUST 5, 1930

Aryl substituted benzoylacrylic acids are readily prepared from maleic anhydride,[1] and dibenzoylethylenes from fumaryl chloride,[2] by the Friedel and Crafts reaction. The products thus obtained are yellow in color, are the stable forms as regards stereochemical rearrangements and undoubtedly possess the *trans* configuration.[1,2,3] The *cis* forms of many unsaturated 1,4-diketones are prepared by the action of sunlight on the *trans* isomers,[2,3] but the corresponding labile *(cis)* isomers of unsaturated 1,4-ketonic acids are known only in the form of their esters.[4] The present investigation was undertaken to add to the available information concerning these compounds, particularly as regards configurations and stereochemistry.

The configurations which were originally assigned to the unsaturated 1,4-diketones seem to be clearly established by the work which has been outlined in earlier papers.[2,3,5] The conclusions are based on two considerations: the relative ease with which the *cis* form reacts with hydrazine to give diphenylpyridazine,[3] and the close analogy between the stability (or rather energy) relationship of these *cis–trans* isomeric pairs[2,3] and that of maleic and fumaric acids.[6] In the preceding paper of this series[7] the validity of evidence based on energy relationship has been confirmed by the determination of the configuration of the analogously related *cis* and *trans* dibenzoyldibromo-ethylenes through the synthesis of the stable *trans* form from dibromofumaryl and *trans* benzoyldibromo-acrylyl chlorides by the Friedel and Crafts reaction, under conditions which preclude the possibility of rearrangements.

The configurations of the unsaturated 1,4-ketonic acids on the other hand are based on very meager evidence. The failure to form naphthoquinones

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[1] H. v. Pechmann, Ber., *15,* 881 (1882), etc. See also Refs. 3 and 4, of the preceding paper.

[2] Conant and Lutz, THIS JOURNAL, *45,* 1303 (1923).

[3] Paal and Schulze, Ber., *35,* 168 (1902).

[4] Rice, THIS JOURNAL, *45,* 222 (1923); see also *ibid., 45,* 232 (1923); *48,* 269 (1926); *50,* 229 (1928).

[5] Lutz, *ibid., 49,* 1106 (1927).

[6] Stoermer, Ber., *42,* 4870 (1909); etc. (The labile *(cis)* isomer has the greater energy content, is formed by the absorption of light energy and rearranges under the influence of catalysts.)

[7] Lutz, THIS JOURNAL, *52,* 3405 (1930).

on dehydration has no bearing on the configuration because of the ease of formation of unsaturated lactones known as "Pechmann dyes"[1] in which the *cis–trans* asymmetry of the double bond is destroyed.[8] The acids, however, do appear to have the *trans* configuration,[1,4,8] and correspond to the yellow stable esters as has been shown by Mrs. Rice,[4] who esterified the silver salt of β-benzoylacrylic acid by means of methyl iodide under conditions which minimize the possibility of rearrangements. During hydrolysis of the isomeric esters, however, rearrangement occurs, since both esters give the same yellow and presumably *trans* acid. On the basis of the energy relationship of the two esters,[4] as compared with that of maleic and fumaric acids,[6] it is highly probable that the stable yellow isomeric esters and the corresponding acids have the *trans* configuration. The hypothetical labile (*cis*) acid must be extremely unstable, since, if it is formed in any reaction (as happens, presumably, in the Friedel and Crafts synthesis from maleic anhydride), it rearranges completely under the experimental conditions. The validity of this reasoning by analogy is now supported by the fact that the chemical reactions of the acid chloride of benzoylacrylic acid are entirely consistent with the conclusions drawn, as will be shown in the discussion to follow.

β-Benzoylacrylic methyl ester (V) has now been prepared from fumaric acid by partial alcoholysis of the acid chloride to the monomethyl ester monochloride (II) followed by a typical Friedel and Crafts reaction (see Diagram 1). Since benzoylacrylic methyl ester has been hydrolyzed to the acid (III),[4] this constitutes another synthesis of the acid from fumaric acid. Since the acid is thus obtainable from both maleic and fumaric acids, a rearrangement occurs in one case, and this undoubtedly in the synthesis from the labile maleic acid as soon as the stabilizing influence of the ring structure of the anhydride disappears in the course of reaction. It would seem highly improbable that the energy relationship would be reversed in going from fumaric acid to benzoylacrylic acid and the configurations must, therefore, correspond in the two cases. The independent evidence necessary to establish this point becomes available through a study of the acid chloride of benzoylacrylic acid.

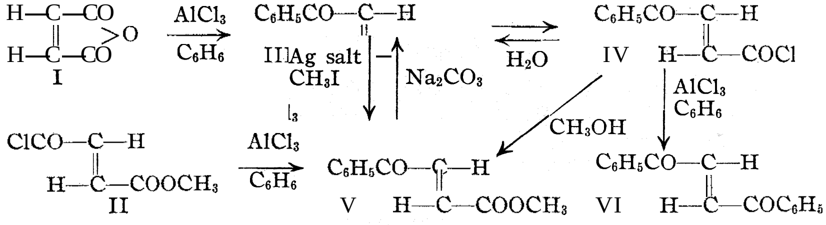

Diagram 1

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[8] (a) Bogert and Ritter, This Journal, 46, 2871 (1924); (b) 47, 526 (1925).

The synthesis of benzoylacrylic acid and its structural relationship to fumaric and maleic acids and the unsaturated 1,4-diketones are outlined in the above diagram. Fumaryl chloride reacts with one equivalent of methyl alcohol to give the monomethyl ester monochloride[9] (11), which may be separated by fractional distillation from unchanged dichloride and from the dimethyl ester which is formed in small amounts. Its structure is shown by its ready reaction with an excess of methyl alcohol to give dimethyl fumarate, and hydrolysis[9] to fumaric monomethyl ester.[10]

β-Benzoylacrylic acid, when treated with one equivalent of phosphorus pentachloride, reacts vigorously to give an oily acid chloride which is very unstable. When heated, or allowed to stand overnight, it decomposes with resinification and the evolution of hydrogen chloride. It could not be distilled or crystallized and, although not obtained in an analytically pure condition, it was isolated sufficiently pure for study by extracting the by-product phosphorus oxychloride with petroleum ether, in which the acid chloride is only slightly soluble.

The structure of β-benzoylacrylyl chloride (IV) and its configurational relationship to the acid and the ester are established by the following facts. The acid chloride is easily hydrolyzed to the original acid when shaken for a short time with water and reacts rapidly with methyl alcohol to give the yellow (stable) methyl ester (V). It is highly improbable that any reversal of configuration could occur in these transformations, and the configuration of the acid, acid chloride and stable (yellow) methyl ester must correspond. Furthermore, the acid chloride reacts readily with aluminum chloride and benzene to give a fair yield of trans dibenzoylethylene (VI). By these reactions it is shown that β-benzoylacrylyl chloride reacts in every way as does a typical normal and active acid chloride. Cis and trans β-benzoyldibromo-acrylyl chlorides have already been prepared;[7] the cis isomer fails to undergo hydrolysis and alcoholysis readily, and with aluminum chloride and benzene reacts exclusively in the pseudo or lactone form, whereas the trans acid chloride behaves in every way normally in these reactions. Inasmuch as β-benzoylacrylyl chloride is of the latter (normal) type, the functional groups must, therefore, lie in a trans relationship.

It is possible, though highly improbable, that benzoylacrylyl chloride, if it were cis, would rearrange in the course of the Friedel and Crafts reaction to give a product derived from the trans configuration, as undoubtedly happens in the preparation of benzoylacrylic acid from maleic anhydride. These two cases are not parallel since in the latter reaction the primary product should be the unstable cis ketonic acid, whereas in the former case, the acid chloride (if cis) should react in the pseudo form to give an unsymmetrical crotolactone as the product. The acid chlorides of succinic[10]

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[9] Anschütz and Baeumges, *Ann.*, 461, 188 (1928).

[10] Sudborough and Roberts, J. *Chem. Soc.*, **87, 1843** (1905).

and dichlorosuccinic[5] acids react tautomerically to give products derived from both the normal and the pseudo dichlorides, but when the functional groups are in actual cis relationship the pseudo or lactone form seems to react exclusively, as happens with phthalyl chloride,[11] o-benzoylbenzoic anhydrides,[12] and cis β-benzoyldibromo-acrylyl chloride.' Maleil chloride has been studied in this connection in a typical Friedel and Crafts reaction, and fails to yield significant amounts of the products to be expected from an acid chloride of normal structure. It seems clear, then, that if the configuration of benzoylacrylic acid were cis, its acid chloride would certainly react in the pseudo or lactone ring form and would not yield significant amounts of dibenzoylethylene in the Friedel and Crafts reaction.

As a consequence of the above considerations it follows that the configurations of the acid and esters as discussed above are confirmed. The stable yellow ester has been obtained from the acid by esterification of the silver salt[4] and is now prepared from the acid chloride by the action of methyl alcohol, and in neither case is rearrangement at all likely. Since the acid is now shown to be trans, it follows that the stable yellow ester is trans, that the labile colorless isomer is cis, and that the relation between stability (or energy content) and configuration corresponds to that for maleic and fumaric acids and the stereoisomeric unsaturated 1,4-diketones.

The synthesis of trans dibenzoylethylene from fumaryl chloride[2] and now from benzoylacrylyl chloride has been repeated under mild conditions and no trace of the labile isomer was isolated from the products. Undoubtedly, as has been shown independently, the configurations of the products correspond to that of the starting material, but this is not proved by the synthesis because the labile isomer (unlike cis dibenzoyldibromo-ethylene[7]) is unstable under the conditions of the Friedel and Crafts reaction and would be largely or completely rearranged if it were formed during the reaction. Cis dibenzoylethylene in benzene is partially isomerized when heated for a short time with aluminum chloride, with which it combines to form a dark red complex compound; however, when it is present during actual reaction between fumaryl chloride, benzene and aluminum chloride, it is practically completely isomerized, and only traces can be recovered. The rearrangement, then, would appear to be facilitated by the evolution of hydrogen chloride during the reaction; but the mechanism does not involve the formation of an intermediate hydrogen chloride addition compound followed by elimination of hydrogen chloride under the influence of aluminum chloride, because this addition compound is known, reacts to give a typical red halochromic salt when heated with aluminum chloride and benzene, and yet is recovered unchanged on subsequent hydrolysis.

The configurations of new derivatives synthesized from trans starting

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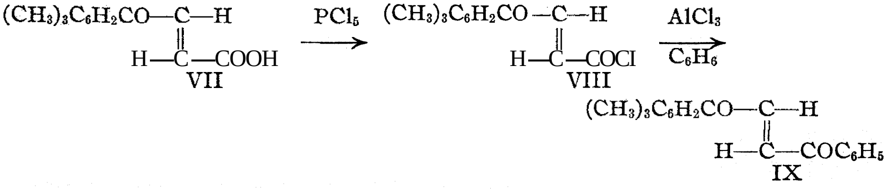
[11] Baeyer, *Ann.*, 202, 50 (1880).

[12] H. v. Pechmann, *Ber.*, 14, 1865 (1881).

materials by the Friedel and Crafts reaction, to be sure, may now be assigned with considerable certainty, but in view of the foregoing discussion it is obvious that proof of configuration in these cases really rests on analogy with products the configurations of which have been determined independently. If the proof of configurations of the various compounds discussed in this and in the preceding paper is accepted, it is noteworthy that without exception the labile stereoisomers of the many and various unsaturated 1,4-dicarbonyl compounds in which the double bond is unsubstituted or is symmetrically disubstituted have the cis configuration. Therefore, one may now safely assign by analogy the configurations of all new derivatives of these types on the basis of synthesis from known stable *trans* compounds or on the basis of lability relationship as compared with that of maleic and fumaric acids. Undoubtedly these considerations apply also to simple unsymmetrically substituted products where hydrogen of the double bond is replaced by groups similar in character to halogen or methyl (*i.e.*, derivatives of citraconic and mesaconic acids, etc.). Experiments are being carried out to test this hypothesis further.

Mesitoylacrylic acid (VII)[13] was found to give a typical acid chloride (VIII) which reacted further with mesitylene and aluminum chloride to give small but significant yields of *trans* dimesitoylethylene. In a limited way it now becomes possible to prepare simple unsymmetrical unsaturated 1,4-diketones. Mesitoylacrylyl chloride (VIII) reacts readily with aluminum chloride and benzene to give benzoylmesitoylethylene (IX, Diagram 2); however, when benzoylacrylyl chloride is used in a similar synthesis with mesitylene and aluminum chloride, only non-crystalline products are obtained. Curiously enough the melting point of the new unsymmetrical product (61.5") is considerably lower than that of either of the two related symmetrical products, dibenzoylethylene (m. p. 111°) and dimesitoylethylene (m. p. 174°). This phenomenon was noted also in the case of the similarly substituted dibromo derivatives,[7] and it would appear that the remarkably lowered melting point is concerned with the unsymmetrical character of the molecule.



$$\begin{array}{c}(CH_3)_3C_6H_2CO—C—H\\ \| \\ H—C—COOH\\ \text{VII}\end{array} \xrightarrow{PCl_5} \begin{array}{c}(CH_3)_3C_6H_2CO—C—H\\ \| \\ H—C—COCl\\ \text{VIII}\end{array} \xrightarrow[C_6H_6]{AlCl_3} \begin{array}{c}(CH_3)_3C_6H_2CO—C—H\\ \| \\ H—C—COC_6H_5\\ \text{IX}\end{array}$$

DIAGRAM 2

The Stereochemical Mode of Addition of Bromine and the Configuration of the Dibromides.—In an earlier paper the stereochemical mecha-

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[13] Kozniewski and Marchlewski. *Bull. Acad. Sci. Cracow,* 81 (1906).

nism of addition of halogen under controlled conditions to dibenzoylethylene[5] was shown to be *trans*, and an important part of the evidence involved the determination of the configurations of the dihalides (XII and XVI) by relating them to the dibromosuccinic acids, the configurations of which are known.[14] In carrying this work further it has been possible to prepare these two dibromides from the two known stereoisomeric normal (X)[15] and iso (XIV)[8b] β-benzoyldibromopropionic acids. The iso acid is the sole product of the Friedel and Crafts reaction on dl-dibromosuccinic anhydride (XIII), and must correspond with it in configuration since there is no reason to suppose that any rearrangement related to the Walden inversion is possible when none of the groups attached to the asymmetric carbon atoms have been replaced in the reaction. The normal benzoyldibromopropionic acid is obtained as the main product of the addition of bromine to benzoylacrylic acid, and since it is the stereoisomeric racemic compound, it must have the opposite configuration (X) corresponding, therefore, to meso dibromosuccinic acid (from which, however, it has not been directly synthesized, although experiments are under way with this in view). The relationships are outlined in Diagram 3.

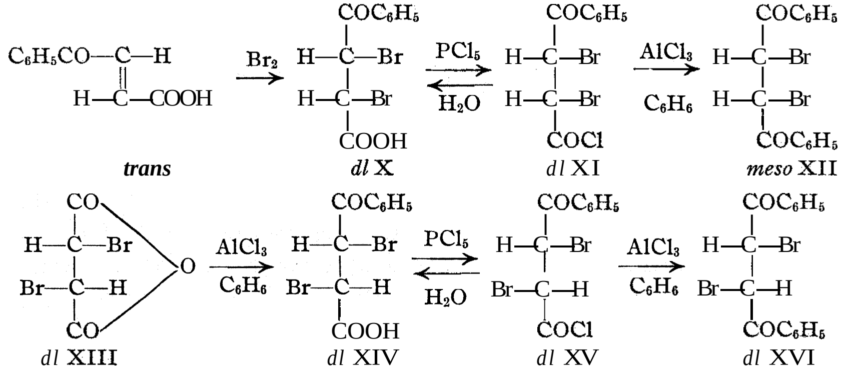

DIAGRAM 3

The two stereoisomeric benzoyldibromopropionic acids (X and XIV) react with phosphorus pentachloride to give oily acid chlorides (XI and XV) which are readily hydrolyzed back to the corresponding acids without change of configuration. These acid chlorides were not isolated in an analytically pure state, as they did not crystallize and decomposed when distilled under diminished pressure. Both acid chlorides reacted with aluminum chloride and benzene to give in each case exclusively a different dibenzoyldibromo-ethane, the chloride of the normal acid (XI) giving a good yield of the meso product (XII), and the iso acid chloride (XV) a

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[14] (a) McKenzie, J. *Chem. Soc.*, *101*, 1196 (1912); (b) Holmberg, *Svensk. Farm. Tid*, 24, 105 (1912).

[15] Ref. 1 and also Bougault, *Ann. chim. phys.*, [8] *15*, 491 (1908).

rather low yield of the dl-isomer (XVI). In each case no trace of the compound of opposite configuration was isolated. The two possible products crystallize well and are easily separated. If both had been formed in a reaction in significant amounts they would have been detected. It seems clear, therefore, that in each series of compounds there is a correspondence of configuration, as is indicated in Diagram **3.**

The mechanism of the addition of bromine to unsaturated 1,4-ketonic acids may be deduced from these relationships because the configurations of both starting material and addition products are now reasonably well established. Benzoylacrylic acid has been shown to add bromine to give mainly the normal dibromide (X), which has a melting point nearly identical with that of the isomeric iso benzoyldibromopropionic acid (XIV), which is obtained from dl-dibromosuccinic anhydride. Since the bulk of the product is the normal dibromide and since this dibromide corresponds in configuration to meso dibenzoyldibromo-ethane, then the stereochemical mode of addition of bromine would appear to be trans. However, in view of the fact that mixtures of isomeric dibromides are invariably obtained (contrary to Bogert and Ritter[8b]), and since the iso dibromide is obtained under some conditions in very considerable yield (see experimental part and also the recent work of Mrs. Rice[16]), no conclusion can be drawn as yet. Cis and trans dibenzoylethylenes undergo trans addition of bromine only under certain controlled conditions,[5] and ordinarily give mixtures of stereoisomeric dibromides, as is the case with benzoylacrylic acid. The results of this paper, through the determination of configurations of the substances concerned, open the way to further profitable study, and experiments are in progress on the acid and on the esters where both cis and trans isomers are available, in order to gain further information on the mechanism of addition under conditions which will permit consistent stereochemical orientation during reaction.

Stereochemical Mode of Addition of Halogen to **Dibenzoylacetylene.**—In an earlier research[17] halogens were found to add to dibenzoylacetylene to give in each case largely the labile stereoisomeric dihalide. It was pointed out that if these labile isomers were cis, then the stereochemical mechanism of the addition to dibenzoylacetylene is cis. The configurations hypothesized have now been shown to be correct[7] by the synthesis of trans dibenzoyldibromo-ethylene from trans benzoyldibromo-acrylic acid and from dibromofumaric acid. As a consequence the cis mechanism of addition is definitely substantiated. It would seem, then, that the normal mode of addition of halogen to the acetylene linkage, when conditions are such as to *permit* molecular orientation during reaction, is cis, and opposite in a stereochemical sense to the normal (trans) mode of addition of halogen

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[16] **Rice,** THIS JOURNAL, **52,** 2098 (1930).

[17] Conant and Lutz, *ibid.*, **47,** 881 (1925).

to the ethylene double bond. Problems in this field are being actively investigated in this Laboratory.

Experimental Part

Fumaryl Chloride.—Boiling point 59° under 16 mm. pressure (Anschütz and Wirtz[18] found 60° at 14 mm.).

Fumaric Monomethyl Ester Monochloride.—The method of Anschütz and Baeumges[9] was modified. A slight excess of one equivalent of methyl alcohol (13 g.) in 200 cc. of benzene was added slowly to 60 g. of well-stirred fumaryl chloride, and the mixture was allowed to stand for five hours. During the addition of methyl alcohol heat and hydrogen chloride were evolved. The bulk of the product distilled at 76° under 22 mm. pressure; crude yield, 30 g. The residue in the flask solidified and was identified as dimethyl fumarate. The crude product was fractionally distilled under diminished pressure using a 10-inch Vigreaux column. A small amount of fumaryl chloride distilled first. The bulk of the material was collected in a series of fractions which solidified on cooling in ice, and which melted at points ranging from 13 to 16°. The two fractions melting sharply at 16° were chosen for analysis.

They gave colorless needles; melting point 16° (corr.); boiling point 69.5° (corr.) at 14 mm. pressure; insoluble in cold petroleum ether.

Anal. Calcd. for $C_5H_5O_3Cl$: Cl, 23.87. Found: 23.62.

Fumaric Acid Monomethyl Ester.—Fumaric monomethyl ester monochloride was shaken with water. The emulsion which formed quickly crystallized to give a nearly quantitative yield of fumaric acid monomethyl ester[9,18] which was recrystallized from benzene and obtained as feathery white crystals melting at 144.5° (corr.) and was identified by analysis.

Anal. Calcd. for $C_5H_6O_4$: C, 46.92; H, 4.62. Found: C, 47.04; H, 4.20.

Trans **β-Benzoylacrylic Acid Methyl Ester (V).**—The ester was prepared by the Friedel and Crafts reaction with aluminum chloride and benzene on pure fumaric monomethyl ester monochloride, or directly on the crude mixture obtained by the action of one equivalent of methyl alcohol on fumaryl chloride.

In a typical experiment 1.5 g. of fumaric monomethyl ester monochloride in 5 cc. of benzene was treated with 3 g. of aluminum chloride.[19] The mixture was heated on a water-bath for ten minutes and was then decomposed in ice and hydrochloric acid. The benzene layer was distilled under diminished pressure and gave 1.5 g. of nearly pure benzoylacrylic acid methyl ester melting at 29° and boiling at 168° under 17 mm. pressure.

In another experiment a benzene solution of 5.5 g. of methyl alcohol was added slowly over a period of one hour to 25 g. of fumaryl chloride. After standing for four hours the mixture was refluxed for three minutes. It was then treated directly with 75 g. of aluminum chloride added in small portions with vigorous mechanical stirring. After the addition of the first third of the aluminum chloride the mixture turned brown. Heat and hydrogen chloride were evolved up to the addition of the last portion of aluminum chloride. The mixture was then decomposed in the usual way, and the benzene layer was distilled under diminished pressure. Some dimethyl fumarate was obtained in the first fraction; then 20.5 g. of benzoylacrylic methyl ester melting at 28–29° distilled; yield, 67%. A red tarry residue remained. When, in another experiment,

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[18] Anschütz and Wirtz, *Ber.*, 18, 1947 (1885).

[19] In this and in similar experiments a high grade of finely ground anhydrous aluminum chloride was used.

the benzene solution was evaporated and diluted with petroleum ether, a small yield of *trans* dibenzoylethylene was obtained. The benzoylacrylic methyl ester was identified by a mixed melting point with known material, by conversion into the *cis* isomer in the sunlight,[4] and by its reaction with semicarbazide.[4]

***Trans* β-2,4,6-Trimethylbenzoylacrylic** Acid **Methyl** Ester, $(CH_3)_3C_6H_2COCH{=}CHCOOCH_3$.—A solution of fumaric monomethyl ester monochloride, prepared by the action of 6.5 g. of methyl alcohol in 75 cc. of carbon disulfide and 24 g. of mesitylene on 30 g. of fumaryl chloride, was treated directly with 90 g. of aluminum chloride, added in small portions with efficient stirring. The red pasty mass was heated for ten minutes and decomposed in ice and hydrochloric acid. The carbon disulfide layer was diluted with ligroin, cooled and seeded. There was deposited 2 g. of nearly pure *trans* dimesitoylethylene. The filtrate was distilled under diminished pressure. The first fraction consisted of mesitylene, dimethyl fumarate and a small amount of unchanged fumaric monomethyl ester monochloride; 8 g. of yellow oil then distilled at 152–160° under 18 mm. pressure, and solidified on cooling; yield, 18%; pale yellow, rectangular, truncated tablets; melting point 53° (corr.) after repeated crystallization from petroleum ether; soluble in alcohol, ether, benzene, acetone, ethyl acetate, acetic acid and chloroform.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.40; H, 6.94. Found: C, 72.22; H, 6.93.

β-2,4,6-Trimethylbenzoylchloropropionic Methyl Ester, $(CH_3)_3C_6H_2COCH_2CHClCOOCH_3$.—A solution of 2 g. of *trans* β-mesitoylacrylic acid in methyl alcohol was saturated with dry hydrogen chloride, and allowed to stand overnight. On decomposing in ice and sodium carbonate an oil was obtained which quickly crystallized; yield, 2 g. The position of the chlorine atom was not determined.

It forms colorless crystals; melting point 78° (corr.) after repeated crystallization from ligroin.

Anal. Calcd. for $C_{14}H_{17}O_3Cl$: C, 62.56; H, 6.38; Cl, 13.20. Found: C, 62.29; H, 6.38; Cl, 12.72.

***Trans* β-Benzoylacrylyl** Chloride (IV), $C_6H_5COCH{=}CHCOCl$.—Benzoylacrylic acid, when treated with one equivalent of phosphorus pentachloride, reacts vigorously with the evolution of heat and hydrogen chloride. The product is a yellow oil. If the temperature of the reaction is not moderated the product is dark in color. If the reaction is carried out in solvents, the hydrogen chloride evolved adds to unchanged benzoylacrylic acid to form benzoylchloropropionic acid. This happens also when thionyl chloride is used. The reaction proceeds smoothly on a small scale when the acid and phosphorus pentachloride are mixed with thorough cooling in an ice-bath. When the crude mixture is shaken with water, the phosphorus oxychloride is quickly removed and the acid chloride separates as an oil which may be drawn off. On standing with water it soon hydrolyzes to benzoylacrylic acid hydrate, which was identified in a typical experiment. The crude acid chloride may be separated from the phosphorus oxychloride by extracting the latter with several portions of petroleum ether, but the yield of oily acid chloride is small because it is somewhat soluble in the petroleum ether–phosphorus oxychloride layer.

Benzoylacrylyl chloride is a pale yellow oil. If it is allowed to stand overnight, or is warmed, it decomposes with the evolution of hydrogen chloride and the formation of a hard resinous mass. For this reason it has not been possible to distil it under diminished pressure. Because of its instability it is always freshly prepared for each experiment and is used immediately, usually without removing the phosphorus oxychloride.

Alcoholysis.—The crude benzoylacrylyl chloride from 9 g. of the acid and one equivalent of phosphorus pentachloride **was** poured into methyl alcohol. Heat was evolved. The mixture was immediately decomposed in ice and the oil was extracted with chloroform and distilled under diminished pressure. The yield of *trans* benzoylacrylic methyl ester boiling at 150° under 5 mm. pressure was 5 g. (52%).

Dibenzoylethylene (VI).—A crude mixture of benzoylacrylyl chloride and phosphorus oxychloride from 2.64 g. of the acid and 3.5 g. of phosphorus pentachloride was treated with 30 cc. of benzene and 15 g. of aluminum chloride. Heat and hydrogen chloride were evolved. The red mixture was decomposed immediately in ice and the mixture was stirred with water to decompose the phosphorus oxychloride. The dark colored benzene layer was allowed to evaporate and the black residue was taken up in alcohol. A black crystalline deposit was filtered off, washed with alcohol and crystallized from benzene and then from alcohol. The dark color was largely removed and 0.8 g. of pale yellow needles melting at 110° was obtained and identified by a mixed melting point as dibenzoylethylene. From the filtrates 0.75 g. of very dark colored crystals was obtained and identified as nearly pure material melting at 107–108°. The total yield of nearly pure dibenzoylethylene was 1.55 g. (44%).

The experiment was repeated several times and the results were thoroughly substantiated. A black tar was obtained as by-product.

Action of Aluminum Chloride on *Cis* **Dibenzoylethylene.**—One gram of *cis* dibenzoylethylene was treated with 10 cc. of benzene and 2 g. of aluminum chloride. A red gummy mass formed immediately and gave a deep red solution when the mixture was heated to boiling. The product was decomposed in ice and fractionally crystallized by successive additions of petroleum ether to the benzene solution, followed by cooling and evaporating. The first two fractions (0.35 g.) proved to be unchanged *cis* dibenzoylethylene, and the third fraction and the residue (0.55 g.) consisted mainly of *trans* dibenzoylethylene.

The experiment was repeated using 20 cc. of benzene and 3 g. of aluminum chloride, and refluxing for ten minutes. The product was found to be largely the *trans* isomer, but an appreciable amount of the *cis* isomer (about 10%) was recovered.

A synthesis of *trans* dibenzoylethylene was carried out in which the fumaryl chloride was added to a cooled mixture; the temperature was not allowed to go above 50° and the total time of reaction was about one minute. The yield (65%) was low because the reaction was not complete, as was shown by the odor of fumaryl chloride after decomposing in ice. No *cis* isomer was isolated or detected among the products. In two similar experiments to which samples of *cis* dibenzoylethylene had been added, the *cis* isomer was completely isomerized in one case, and very nearly so in the other (a trace being recovered).

Trans **β-2,4,6-Trimethylbenzoylacrylyl** Chloride (VIII), $(CH_3)_3C_6H_2COCH{=}CH{-}COCl$.—Equivalent amounts of *trans* β-mesitoylacrylic acid and phosphorus pentachloride were mixed with cooling in an ice-bath. Hydrogen chloride was evolved and the mixture liquefied. The heat of reaction was moderated to prevent the formation of a dark colored product. In the experiments to follow (hydrolysis, alcoholysis, and the Friedel–Crafts reaction) the acid chloride was not separated from the by-product phosphorus oxychloride. The acid chloride is an unstable yellow oil which resembles benzoylacrylyl chloride in its properties.

The crude acid chloride from 0.5 g. of acid was shaken for several hours with water and the resulting yellow solid was filtered, washed with petroleum ether and identified as mesitoylacrylic acid; yield, 0.4 g.

The crude acid chloride from 1 g. of acid was added to methyl alcohol. The solution was immediately decomposed in ice and extracted with ether. On evaporating the solvent, treating the oily residue with petroleum ether and cooling, 0.15 g. of yellow crystals was obtained and identified as *trans* mesitoylacrylic methyl ester.

Trans **Di(2,4,6-trimethylbenzoyl)ethylene.**—In a typical experiment 2 18 g. of β-mesitoylacrylic acid was treated with 2.1 g. of phosphorus pentachloride. The mixture containing the crude acid chloride was then treated directly with 1.5 g. of mesitylene, 10 cc. of carbon disulfide, and 6 g. of aluminum chloride, and was decomposed in ice and worked up in the usual manner. A small yield (0.15 g.) of yellow crystals was isolated and identified as dimesitoylethylene. The reaction was repeated several times without bettering the yield. The principal product was an orange colored resinous oil.

In a similar experiment benzene was used as the solvent in place of carbon disulfide. The product was separated from an orange colored resin by taking up in petroleum ether. The crystalline product was warmed with methyl alcohol and on cooling 0.55 g. of yellow crystals was isolated and identified as nearly pure *trans* dimesitoylethylene (yield, 16.5%). The methyl alcohol filtrate was diluted with water and gave 0.35 g. of colorless crystals melting at 217°. The new substance dissolved in sodium carbonate and was precipitated by acids. The experiment was repeated and the yield of *trans* dimesitoylethylene was confirmed, but only 0.1 g. of the colorless acid was isolated. The latter substance will be investigated further.

Normal and Iso **β-Benzoyldibromopropionic** Acids (X and **XIV**).—The iso acid was prepared by the method of Bogert and Ritter[8b] by adding aluminum chloride to a cooled mixture of benzene and dibromosuccinic anhydride.

The normal acid was prepared by adding one equivalent of bromine to *trans* benzoylacrylic acid, in acetic acid as the solvent. Recrystallization from toluene gave a product melting at 148° (decomp.).

In two experiments one equivalent of bromine in 6 cc. of chloroform was added to 1 g. of benzoylacrylic acid in 5 cc. of chloroform. In the first case the reaction mixture was kept at the boiling point of chloroform. On evaporating the solvent and crystallizing the somewhat oily residue from benzene a yield of 1.3 g. of pure acid melting at 148° was obtained. In the second experiment the reaction mixture was cooled in an ice-bath. Upon evaporation of the solvent, the residue completely crystallized, melted at 108–135° (yield 1.8 g.) and was shown to consist of a mixture of the two isomeric benzoyldibromopropionic acids as follows. A dilute chloroform–benzene solution of the mixture was allowed to evaporate slowly overnight, and a deposit of large crystals was obtained from which the mother liquor was decanted. The crystalline layer adhering to the bottom of the dish was washed with ligroin. The large opaque granules of twinned rhombic plates were dislodged and rolled out of the thin layer of smaller, clear, rhombic plates which adhered firmly to the bottom of the vessel. Thus complete separation of the pure components was effected; the former melted with decomposition at 149° and was identified as the iso acid; the latter, melting at 148° (decomp.), was shown to be the normal acid; a mixture of the two melted at 108–135°. The disagreement as to the melting points[20] is perhaps not surprising since both products decompose at their melting points.

Normal and Iso **β-Benzoyldibromopropionyl** Chlorides (XI and XV), C_6H_5-COCHBrCHBrCOCl.—The acid chlorides were obtained as oils by the action of an excess of phosphorus pentachloride on the acids. They decomposed with the evolution of hydrogen chloride when distillation under diminished pressure was attempted. Samples of the oily acid chlorides, suspended in water, were allowed to stand overnight and hydrolyzed to give nearly quantitative yields of the original acids.

dl-Dibenzoyldibromo-ethane (XI).—The crude acid chloride from 3 g. of iso β-

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[20] For the normal acid H. v. Pechmann[1] gives 135°, Bougault [*Ann. chim. phys.*, [8] *15*, 491 (1908)] 148°, Mrs. Rice[16] 150°, my finding 150° (corr.) with decomposition; for the iso acid Bogert and Ritter[8b] give 142°, Mrs. Rice[16] 148°; my finding 150° (corr.) with decomposition.

benzoyldibromopropionicacid and 3 g. of phosphorus pentachloride was treated directly with benzene and 15 g. of aluminum chloride. Heat and hydrogen chloride were evolved. The mixture was then decomposed in ice. The benzene layer was evaporated and the residue taken up in methyl alcohol; 0.8 g. of crystals was isolated and identified by a mixed melting point as nearly pure dl-dibenzoyldibromo-ethane. The tar obtained by diluting the filtrate with water was taken up in petroleum ether. The solution deposited 0.4 g. of colorless crystals of a new substance melting at 155–160° which was soluble in sodium carbonate and was precipitated by acids. The yield of *dl*-dibenzoyldibromo-ethane was confirmed in several experiments, but only traces of the new acid were obtained. The latter will be investigated further.

Meso Dibenzoyldibromo-ethane (XVI).—The crude acid chloride from 1.5 g. of β-benzoyldibromopropionic acid and phosphorus pentachloride was treated directly with benzene and 6 g. of aluminum chloride; the mixture was then decomposed in ice. The benzene layer was cooled and diluted with a little petroleum ether. The crystalline deposit was washed with sodium carbonate solution. The product melting at 176° (decomp.) was identified as meso dibenzoyldibromo-ethane; yield, 1.0 g. (57%).

A Third Isomeric β-Benzoylbromo-acrylic Acid, $C_6H_5COCH{=}CBrCOOH$ or $C_6H_5COCBr{=}CHCOOH$.—In an attempt to prepare benzoylpropiolic acid, a mixture of *25* g. of β-benzoyldibromopropionic acid, 30 g. of sodium acetate. 7 g. of sodium carbonate, 150 cc. of acetone and 10 cc. of methyl alcohol was refluxed for four and one-half hours. After cooling, the crystalline solid was filtered off and acidified. The crystalline product obtained was identified as nearly pure β-benzoyl-β-bromo-acrylic acid (known[8b,16]) melting at 106–107°. The acetone filtrate was acidified and diluted with water, and gave 1.5 g. of a new isomeric β-benzoylbromo-acrylic acid. This new substance gave a considerable melting point depression when mixed with the @-bromo isomer prepared by Bogert and Ritter,[8b] differs in melting point from the α-bromo derivative obtained by Mrs. Rice,[16] and is undoubtedly a stereoisomer of one of these; colorless needles; melting point 105° (corr.) after several crystallizations from benzene and petroleum ether.

Anal. Calcd. for $C_{10}H_7O_3Br$: Br, 31.34. Found: 31.65.

A small sample reacted with zinc and acetic acid with the evolution of heat. On filtering, diluting with water, extracting with ether, evaporating and crystallizing from water, shiny plates of benzoylpropionicacid were isolated and identified.

The position of the bromine atom and the configuration have not been determined.

On the Preparation of Some Unsaturated 1,4-Diketones and their Derivatives.—In the Friedel and Crafts reactions used in the foregoing work it was often found desirable to use the crude acid chloride without removing the phosphorus oxychloride obtained as a by-product of the action of phosphorus pentachloride on the acids. Experiment showed that in the synthesis of dibenzoylethylene from fumaryl chloride the yield was in no way affected by the presence of phosphorus oxychloride, providing that a large excess of aluminum chloride was used. It was necessary, however, to insure complete hydrolysis of the phosphorus oxychloride after decomposing in ice, before evaporating the benzene solution of the product; otherwise a dark color developed. It was also found that an excess of aluminum chloride in general gives a better yield and a purer product, and that the reaction is complete in a very short time. The dark red color that often develops in the final product seems to be due to the action of unchanged or partly reacted acid chloride or phosphorus oxychloride which escapes hydrolysis and remains in the benzene solution of the final product. Two typical experiments follow in outline.

(a) Fumaryl chloride (15 g.) was added rapidly drop by drop to a well-stirred mixture of 200 cc. of benzene and 45 g. of aluminum chloride. Considerable heat and hydrogen chloride were evolved. In a few minutes the reaction subsided and the red pasty mass was decomposed and the product isolated in the usual manner; the yield of pure *trans* dibenzoylethylene melting at 108–108.5° was 21 g. (89%).

(b) In a similar experiment 15 g. of fumaryl chloride in 20 g. of phosphorus oxychloride was added to a mixture of 60 g. of aluminum chloride in benzene. After decomposing in ice, the mixture was stirred for half an hour with water to decompose completely the phosphorus oxychloride; the yield of pure *trans* dibenzoylethylene was 21.5 g. (93%).

The use of carbon disulfide as the solvent in these Friedel and Crafts reactions often gives very poor results, and in many cases the yields are very considerably improved by using benzene instead. This method was applied successfully in some reactions between fumaryl chloride and certain aromatic hydrocarbons possessing a much greater reactivity than benzene, namely, mesitylene and naphthalene. When technical benzol, which contains as much as 20% of toluene, is used in the reaction, the product is exclusively *trans* ditoluylethylene. The use of benzene as the solvent is particularly good in the preparation of *trans* dimesitolylethylene, whereby a yield of 74% was obtained in a typical experiment. The yield of *trans* dinaphthoylethylene is very low when carbon disulfide is used as the solvent,[17] but it has been raised to 41% in a typical experiment when the reaction was carried out in benzene as the solvent, under somewhat moderated conditions. Curiously, however, the method failed to improve the yield of *trans* dianisoylethylene. Furthermore, in certain experiments using dibromofumaryl, β-benzoyl- and β-mesitoyl-dibromo-acrylyl chlorides[7] it was found that the benzene used as the solvent reacted instead of the mesitylene, a result contrary to that which was expected from the above results with fumaryl chloride.

Di(α-naphthoyl)ethane, $C_{10}H_7COCH_2CH_2COC_{10}H_7$.—Dinaphthoylethylene (2 g.) was reduced in the usual way with zinc and acetic acid; the yield of ethane was 1.5 g.; shining, colorless leaflets (microscopic scales); melting point 130–131° (corr.); difficultly soluble in boiling alcohol; soluble in chloroform, acetone, benzene, ethyl acetate, and acetic acid; insoluble in ether and ligroin.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.12; H, 5.36. Found: C, 85.02; H, 5.39.

***dl*-Di(4-methylbenzoyl)dibromo-ethane,**[21] $CH_3C_6H_4COCHBrCHBrCOC_6H_4CH_3$.—*Trans* ditoluylethylene adds bromine in acetic acid to give mainly the high-melting meso[22] dibromide melting at 198". The low-melting (*dl*)[22] isomer was isolated in a small yield from the acetic acid mother liquors by diluting with water. It forms fine colorless crystals; melting point 138° (corr.) after repeated crystallization from alcohol and from benzene; soluble in chloroform and hot acetic acid; insoluble in ligroin.

Anal. Calcd. for $C_{18}H_{16}O_2Br_2$: Br, 37.70. Found: 37.55.

Trans **Di(4-phenoxybenzoyl)ethylene,**[21] $C_6H_5OC_6H_4COCH{=}CHCOC_6H_4OC_6H_5$.—Diphenyl ether was allowed to react in the usual way with aluminum chloride and fumaryl chloride in carbon disulfide as the solvent. The product was isolated from a crude resinous tar by crystallizing from acetone and refluxing in solvents with animal charcoal.

It gives orange crystals; melting point 170.5–171° (corr.), after eight crystallizations from an alcohol–benzene mixture; soluble in chloroform, benzene and in hot acetone and acetic acid; insoluble in hot alcohol.

Anal. Calcd. for $C_{28}H_{20}O_4$: C, 80.00; H, 4.80. Found: C, 79.88; H, 4.89.

Trans **Di(4-phenoxybenzoyl)ethane,**[21] $C_6H_5OC_6H_4COCH_2CH_2COC_6H_4OC_6H_5$.—The corresponding ethylene was reduced in the usual way with zinc and acetic acid.

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[21] Prepared and analyzed in this Laboratory by Mr. Ernly Estes.

[22] The configuration is based on analogy (see Ref. 5).

It forms colorless crystals; melting point 160° (corr.) after repeated crystallization from acetone; soluble in chloroform and benzene; insoluble in alcohol.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.57; H, 5.76. Found: C, 79.45; H, 5.11.

Trans **1-Benzoyl-2-(2,4,6-trimethylbenzoyl)ethylene** *(IX)*, $C_6H_5COCH{=}CHCOC_6H_2(CH_3)_3$.—The crude acid chloride from 2.18 g. of *trans* mesitoylacrylic acid and 2.1 g. of phosphorus pentachloride was treated directly with benzene and 8 g. of aluminum chloride. Heat and hydrogen chloride were evolved. The red mass was decomposed in ice. The benzene layer was evaporated and the residue was dissolved in methyl alcohol. On cooling 0.9 g. of pure product was obtained, a yield of 32%.

Anal. Calcd. for $C_{19}H_{18}O_2$: *C*, 82.00; H, 6.52. Found: C, 82.10; H, 6.62.

Benzoylacrylyl chloride when treated with mesitylene and aluminum chloride in carbon disulfide failed to yield a crystalline product.

Reduction with zinc and acetic acid gave a nearly colorless oil which has not yet been obtained in a crystalline form.

Maleil chloride's was prepared by the action of phosphorus pentachloride on maleic acid, and was isolated by fractional distillation under reduced pressure. On redistillation it boiled at 65° under 2 mm. pressure.

Trans **4,4-Diphenyl-4-hydroxybutenoic** Acid, $(C_6H_5)_2C(OH)CH{=}CHCOOH$.—Maleil chloride was used in the Friedel and Crafts reaction with aluminum chloride and benzene under a variety of conditions. Resins were obtained from which small amounts of an acid were isolated as white powdery deposits from carbon tetrachloride solutions. It was soluble in sodium carbonate and precipitated by acids. It formed colorless, microscopic, blade-shaped scales; melting point (decomp.), 224° (corr.) after several crystallizations from acetic acid; very soluble in alcohol; insoluble in ethyl acetate benzene, ethyl bromide and ligroin.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.59; H, 5.55. Found: C, 75.27; 75.90; H, 5.07, 5.61.

The *trans* structure is suggested because the product is not the lactone that was expected. The free hydroxy acid, once formed, undoubtedly rearranges under these conditions to the stable *trans* state as happens in the preparation of benzoylacrylic acid from maleic anhydride.

Summary

The configurations of benzoyl and mesitoylacrylic acids are shown to be *trans* by the normal character of their acid chlorides which have been synthesized and converted into the unsaturated 1,4-diketones by the Friedel and Crafts reaction.

Syntheses of unsaturated 1,4-ketonic esters from fumaric monomethyl ester, and new developments in the synthesis of symmetrical unsaturated 1,4-diketones are described.

The configurations of the dibromides of benzoylacrylic acid are determined by the synthesis of one of them from dl-dibromosuccinic acid, and by their conversion through the acid chlorides into the known dibenzoyldibromomethanes.

The stereochemical mode of addition of bromine to ethylene and acetylene linkages is discussed.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

ATTEMPTS TO RESOLVE DERIVATIVES OF FLUORENE. PARA-AMINOBENZOPWENONE HYDRAZONE[1]

BY CHESTER WALLACE BENNETT AND WILLIAM ALBERT NOYES

RECEIVED MAP 31, 1930 PUBLISHED AUGUST 5, 1930

Having failed to resolve 2-amino-9-diazofluorene[2] into its optical isomers, we turned our attention to the resolution of other 2,9-fluorene derivatives. A thorough examination of the literature revealed a single case only in which such a resolution had been attempted. Bader[3] attempted to resolve 2,9-diaminofluorene by the use of *d*-tartaric acid and also by the aldehyde condensation product with d-helecin. Neither of these agents, however, accomplished any separation. Since there is a possibility that other resolving agents might be more effective, it was decided to prepare his diamine and try other active acids. The reduction of 2-nitrofluorenone oxime following his directions gave only very small yields of impure material but the reduction of 2-aminofluorenone hydrazone by means of zinc dust in boiling glacial acetic acid gave, after hydrolysis of the intermediate acetyl derivative (m. p. 219°), an excellent yield of the beautiful crystals of 2,9-diaminofluorene, m. p. 160°, as described by Bader. The diamine could not be resolved by means of d-camphor sulfonic acid, *d*-phenylaminoacetic acid, nor d-hydroxy-methylene camphor.

Schmidt and Stiitzel had found[4] that the nitration of 9-acetaminofluorene by means of boiling nitric acid yielded 1,8-dinitrofluorenone, m. p. 197–198°, instead of the 1-nitro-9-acetaminofluorene desired. Modifications of their procedure in an attempt to obtain the desired derivative resulted in the formation of light yellow crystals, m. p. 236–238°. From the analyses, which were not wholly satisfactory, it appeared that the material was 1,8-dinitro-9-acetaminofluorene. Since this compound would be symmetrical, it was not further studied.

The resolution of 2-amino-9-hydroxyfluorene was also attempted by means of d-camphor sulfonic acid but no separation could be obtained.

Bader explained his inability to resolve 2,9-diaminofluorene by a rather novel theory based on an assumption that optical isomers do not exist in the case of this compound due to a mutual repulsion between the two amino groups which destroys the tetrahedral arrangement. Since there is no experimental basis for such an assumption, it seems just as likely that the failure to resolve this series of compounds is due to the fact that the right conditions have not yet been found, instead of an inherent lack of isomerism.

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[1] Abstract of portions of a thesis submitted by C. W. Bennett in partial fulfilment of the requirements for the degree of Ph.D. at the University of Illinois.

[2] Bennett and Noyes, *Rec. trav.* **chim.**, 48, 895–898 (1929).

[3] Bader, "Zur Stereochemie des Fluorens," Dissertation, Vienna, 1926, pp. **53–54.**

[4] Schmidt and Stiitzel, ***Ann.*, 370,** 140 (1909).

These results have an interesting bearing on the fact that 2-amino-9-diazofluorene could not be resolved. Since none of the fluorene derivatives have been resolved, it is evident that resolution in this series is, at least, very difficult and the possibility of resolving such a derivative as the diazo compound would necessarily be remote. These results do not prove that the diazo carbon atom is not asymmetric in this compound nor that diazo compounds having an amino group in the molecule cannot be resolved.

In connection with these results, the fact that no substituted diphenylmethane derivatives of the type, $C_6H_5CHX\text{-}C_6H_4\text{-}Y$, have ever been resolved is of interest. Billon[5] has studied this problem and has so far been unsuccessful. Betti[6] and Berlingozzi[7] have, however, resolved a-naphtholphenylaminomethane and naphthylphenylaminomethane, respectively.

In an effort to obtain such a diazo derivative, the synthesis of p-aminophenyl phenyldiazomethane was attempted. The oxidation of p-aminobenzophenone hydrazone gave a beautiful purple solution which undoubtedly contains the diazo derivative but the latter was so unstable that only the ketazine of *p*-aminobenzophenone could be isolated.

Experimental Part

Preparation of **2-Aminofluorenone.**—A suspension of 22.5 g. of 2-nitrofluorenone in 150 cc. of 95% alcohol with 0.2 g. of platinum oxide catalysts was shaken in a bottle with hydrogen under pressure until there was no more absorption. Reduction was quite rapid and beautiful crystals of the amine were obtained. The suspension was heated to boiling and filtered to remove the catalyst and any unreacted nitrofluorenone. The product was purified by dissolving in hot dilute hydrochloric acid and reprecipitating with ammonia. The yield was 18.7 g. or 95% of the theoretical as compared with about 65%, the yield obtained by the use of ammonium sulfide, which is the only method described in the literature.[9] The purple crystals melt at 160°.

Preparation of **2,9-Diaminofluorene.**—Bader's[3] method of reducing 2-nitrofluorenone oxime with zinc dust and hot glacial acetic acid yielded only a small amount of impure material. The reduction of 2-aminofluorenone hydrazone in the same manner, however, gave an excellent yield of the diamine.

Zinc dust was added gradually to a boiling solution of 5 g. of the hydrazone in 100 cc. of glacial acetic acid. After two hours the solution was completely decolorized and reduction was complete. The zinc was removed by filtration and ammonium hydroxide added to the cooled filtrate until alkalinity was reached. The resulting white precipitate was recrystallized from acetone, giving white needles, m. p. 219°. The crude material after refluxing for two hours with 20% hydrochloric acid and treating with norit was filtered and cooled. When ammonium hydroxide was added, beautiful silvery flakes were formed, m. p. 156°. Recrystallization from toluene yielded crystals melting at 160" as described by Bader. The first material was apparently the monoacetyl derivative of the diamine and resulted from the boiling with glacial acetic acid.

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[5] Billon, *Ann. chim.*, [10] *7*, 314, 384 (1927).

[6] Betti, *Gazz. chim. ital.*, *37, I*, 62 (1907).

[7] Berlingozzi, *ibid.*, 50, 11, 281 (1920).

[8] Voorhees and Adams, THIS JOURNAL, 44, 1397–1405 (1922).

[9] Diels, *Ber.*, 34, 1760 (1901).

Anal. Calcd. for $C_{15}H_{14}N_2O$: N, 11.7. Found: N, 11.6.

The material melting at 160° was in all respects similar to Bader's 2,9-diaminofluorene and the synthesis and analysis prove that to be the correct formula; yield, 4.2 g., or 92.5% of the theoretical.

Anal. Calcd. for $C_{13}H_{12}N_2$: N, 14.29. Found: N, 14.4.

The diamine could not be resolved with d-camphor sulfonic acid, which gave a salt with a specific rotation of +15.05' for all fractions, the hydrolyzed amine from which was inactive. No salt was formed with *d*-phenylaminoacetic acid and the d-hydroxylmethylene camphor derivative could not be crystallized.

Nitration of 9-Acetaminofluorene.—Fluorenone oxime, prepared by the action of potassium ethylate on a mixture of amyl nitrite and fluorene according to Wislicenus' and Waldmüller's directions,[10] was reduced by zinc dust and acetic acid to the fluorenylamine by Schmidt and Stutzel's method.[11] Their method of acetylating the amine with acetic anhydride was also used. No nitration occurred when 10 g. of the acetyl derivative was dissolved in 100 cc. of glacial acetic acid and 20 cc. of nitric acid and heated for one hour on the steam-bath. When 6 g. of the acetyl derivative was suspended in 200 cc. of glacial acetic acid and 1.7 g. of nitric acid added, there was no change after two months at room temperature and the acetyl derivative was recovered by the addition of water. Nitration did occur when 10 g. of the acetaminofluorene was added slowly to a mixture of 18 cc. of sulfuric acid and 37 cc. of nitric acid. The product was cooled and poured into ice water. The yellowish mass was recrystallized from boiling glacial acetic acid several times until a stable melting point of 236–238" was obtained. The analysis was not perfectly satisfactory but indicated that the compound was 1,8-dinitro-9-acetaminofluorene. The same compound was also formed when only enough nitric acid was used to obtain the mononitro derivative.

Anal. Calcd. for $C_{15}H_{11}O_5N_3$: C, 57.5; H, 3.51; N, 13.4. Found: C, 58.4; H, 3.79; N, 13.0.

p-Aminobenzophenone Hydrazone.—Phthalanil prepared by Drbner's method[12] of distilling phthalic anhydride and aniline together, was converted into the benzoyl derivative by means of benzoyl chloride and zinc chloride. This material on hydrolysis by Torrey and Rafsky's method[13] gave p-aminobenzophenone, m. p. 124". The hydrazone, which has not been previously described, was prepared by refluxing a mixture of 15 g. of p-aminobenzophenone, 15 cc. of 40% hydrazine hydrate and 50 cc. of 95% alcohol for four days with 10 g. of barium oxide. After this period, the filtered solution yielded yellow needles, m. p. 139–140°.

Anal. Calcd. for $C_{13}H_{13}N_3$: N, 19.91. Found: N, 20.2.

The filtrate on evaporation yielded a mixture of the new hydrazone and a yellow powder, m. p. 225°, which was shown to be the ketazine of p-aminobenzophenone. The same material was formed when a vacuum distillation of the hydrazone was attempted and also if the hydrazone was recrystallized too many times. Refluxing of the ketazine with 40% hydrazine hydrate solution and barium oxide gave no apparent change.

Anal. Calcd. for $C_{26}H_{22}N_4$: N, 14.3. Found: N, 14.01.

Attempts to oxidize the hydrazone to the diazo compound using mercuric oxide and mercuric acetamide in various solvents gave a purple solution from which the diazo derivative could not be isolated but instead the ketazine was obtained as its decomposition product.

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[10] Wislicenus and Waldmuller, ***Ber.***, 41, 3334–3340 (1908).

[11] Schmidt and Stutzel, ibid., 41, 1246 (1908).

[12] Döbner, *Ann.*, 210, 267 (1881).

[13] Torrey and Rafsky, THIS JOURNAL, **32,** 1489 (1910).

Summary

1. New syntheses for 2,9-diaminofluorene and for 2-aminofluorenone have been developed. Neither the diamine nor 2-amino-9-hydroxyfluorene could be resolved.

2. Attempts to prepare 1-nitro-9-aminofluorene by nitration of 9-acetaminofluorene resulted in the formation of a compound which was probably 1,8-dinitro-9-acetaminofluorene, m. p. 236–238°.

3. The failure to resolve any 2,9-fluorene compound may be due to a lack of asymmetry or to the fact that the right conditions have not been found. In any case, the failure to resolve 2-amino-9-diazofluorene does not demonstrate that the carbon atom bearing the diazo group is not asymmetric.

4. *p*-Aminobenzophenone hydrazone, m. p. 139–140°, was prepared along with the ketazine, m. p. 225°. The former, on oxidation, yielded an unstable diazo derivative which could not be isolated.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

A METHOD FOR THE STUDY OF TOXICITY USING GOLDFISH[1]

BY W. A. GERSDORFF

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The use of derris root as a fish poison by the inhabitants of the localities to which this plant is native suggested the use of fishes as test animals in the study of the comparative toxicity of rotenone, an active constituent of that plant, and its derivatives. The goldfish, being a member of the carp family and so at home in sluggish waters, is more adapted to conditions in still water tanks and jars than most of the native fishes. The fact that fishes accustomed to active, cool waters are liable to suffocate when kept in still, comparatively warm water is a factor to be considered. The goldfish is also more easily obtained in large quantity and is inexpensive. The species sold for aquaria, *Carassius auratus*,[2] is the one used here.

In 1915 Pittenger and Vanderkleed[3] and in 1919 Pittenger[4] found that the goldfish was a suitable test animal in the assay of digitalis preparations. In' 1917 Powers[6] reported an investigation testing the validity of this method and the use in general of the goldfish as the test animal in the

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[1] Presented as a part of the Insecticide Symposium before the Division of Agricultural and Food Chemistry at the 77th Meeting of the American Chemical Society, Atlanta, Georgia, April 7 to 11, 1930.

[2] U. S. Dept. of Commerce, Bureau of Fisheries Econ. Circ. No. 68. p. 1 (1929).

[3] Paul S. Pittenger and Chas. E. Vanderkleed, *J. Am. Pharm. Assocn.*, 4, 427–433 (1915).

[4] Paul S. Pittenger, *ibid.*, 8,893–900 (1919).

[5] Edwin B. Powers, Ill. Biol. Mono., 4, No. 2 (1917).

study of toxicity. Powers' inethod was used as a starting point in the work reported in this paper; several changes, however, were deemed advisable.

Rotenone, prepared in this Laboratory from Derris *elliptica*,[6] was used as the toxic material. As this substance is but slightly soluble in water, some organic solvent non-injurious to the fishes had to be used in preparing stock solutions, from which aliquots could be taken to be added to the test solutions. Preliminary experiments were made with acetone, a good solvent for rotenone, to determine its action on the fishes. In a concentration of 2 parts of acetone to 1000 parts of water, fishes showed distress in half an hour. A concentration of 1 part of acetone to 1000 parts of water, however, was found to have no apparent effect on them. Therefore, stock solutions were made with acetone as the solvent of such concentrations that aliquots sufficiently large to be accurate could be taken without making the concentration of acetone in the test solutions greater than 1 part of acetone to 1000 parts of water.

It was found to be very important to use only goldfishes in good condition, those apparently but slightly out of condition always lowering the survival time appreciably. Fishes used in the tests were either taken from a stock tank which was heated to approximately the same temperature as that of the test solutions or allowed to warm up slowly to that temperature before the test was started. This eliminated any ill effect due to sudden change of temperature. This also is very important since a sudden change, either to a higher or lower temperature, may cause sickness and premature death of goldfishes. The difference between the temperature of the test solutions and that of unheated stock tanks with running water was often over 15° in winter.

Aside from any ill effect, sudden changes from lower to higher temperatures often result in marked temporary increase in activity of fishes? In general the rate of metabolism increases with increase in temperature and diminishes with decrease. Wells[7] found that fishes react to so small a variation in the temperature of the surrounding water as 0.1°. It was found early in this experimental work that a varying temperature had considerable effect, thus necessitating the use of a constant temperature for the tests to achieve good comparative results. Small differences in temperature markedly influence the resistance of the fishes; an increase in temperature lowers the survival time, whereas a decrease in temperature raises it. Therefore, a constant temperature bath with a de Khotinsky regulator was used. Since the work was done in summer as well as in winter, it was difficult to maintain a temperature lower than 27°. This temperature therefore was selected as the temperature of the tests. Variation in temperature was usually less than half a degree.

To determine the size of the fishes used, they were at first weighed, hut later were measured linearly from the mouth to the base of the tail, the latter procedure being the shorter. A number of fishes were both weighed and measured so that the weight of a fish could be estimated from the length when desired. Generally the large fish survived longer than the small ones; therefore fishes as nearly uniform in size as possible should be used.

In making the tests the ratio of one liter of solution to each fish was maintained. Some of the tests were carried out in three-liter wide mouthed jars, known as "candy jars," which were found convenient when two liters of solution were used. The rest of the tests, in which six or eight liters of solution were taken, were carried out in three-gallon cylindrical jars.

In determining toxicity, the criterion used was the death point. Osterhout[8] has pointed out that "the relative toxicity of two substances may

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[6] F. B. LaForge and L. E. Smith, THIS JOURNAL, 51,2574–2581 (1929).

[7] Morris M. Wells, Trans. Ill. Acad. Science, 7, 48–59 (1914).

[8] W. J. V. Osterhout, J. Biol. Chem., 23, 67–70 (1915).

depend very largely on the stage of the reaction at which the measurement is made. . . . It is impossible to determine the precise moment of death," since the death curve "approaches the axis asymptotically." He objected to the death point as a perfectly satisfactory criterion of toxicity. The conclusion was soon reached in this work, however, that the death point is a more exact criterion for the goldfish than the loss of equilibrium, cessation of motion, or loss of irritability. No phenomena suitable for use as criteria, as suggested by Osterhout, have been found to appear at definite points along the course of the reaction with goldfishes. Powers came to the same conclusion and used the death point as the criterion. The death point, although not obtainable with precision from the observation of one or two fishes, was determined with fair accuracy when more (usually six to twelve) were used, and could, of course, be found with even greater accuracy by using a larger number

To find the death point of a fish repeated observations were made to follow the course of the action of the toxic material. The fish usually, but not always, after showing its first distress in swimming, suffered a loss of equilibrium, then lost its ability to swim and finally its irritability. From this point on careful observations were repeatedly made of any gill or mouth movements. These movements may be very faint and require close observation; they may, moreover, last for a long time, and the period is important in finding the actual survival time. It was found that when the fishes were taken out after close observation had failed to detect any gill movement whatsoever in one to one and one-fourth minutes and then were dipped into hydrochloric acid (about 1:3) about half were dead and half would still show faint signs of life.

Powers used only two goldfishes in each concentration in determining the survival time. In order to lessen the effect of individual variations in susceptibility, it was deemed advisable in this work to use a larger number of fishes, especially in the longer survival times. Naturally, variations from the mean survival time increased as the mean increased, that is, as the concentration decreased, but the percentage variation was found to be approximately the same.

Powers found that the survival time curve which is plotted by letting the ordinates represent the survival times of the goldfishes and the abscissas represent the concentrations of the test solutions is logarithmic in function. The middle portion, however, where the velocity of fatality (as measured by the reciprocal of the survival time) increases most rapidly with increase in concentration (usually when the survival time is between three-fourths and four hours) approaches an equilateral hyperbola. Therefore, the corresponding portion in the velocity of fatality curve which is drawn with the reciprocals of the survival times as the ordinates approaches a straight line. This straight line, designated the theoretical velocity of fatality curve, when prolonged cuts the x-axis at a point which Powers designated as the theoretical threshold of toxicity. He suggested, for use in determining comparative toxicities, that if a represents this theoretical threshold of toxicity concentration and Θ the angle formed by the theoretical velocity of fatality curve with the x-axis, the toxicity of the substance may be expressed by the formula T (toxicity) $= \sqrt{\tan \Theta / a}$.

Table I shows the results of a typical group of tests with rotenone at one concentration, 0.075 mg. per liter, from which an idea of the reproducibility of the tests may be obtained.

TABLE I

TOXICITY OF ROTENONE TO GOLDFISH AT A CONCENTRATION OF 0.075 MG. PER LITER AND AT 27.0 ± 0.2°

Test no.	Length of fish in millimeters	Weight in grams[a]	Survival time of fish in minutes[b]	100 × the reciprocal of the survival time
1	42	2.3	93−	1.08
2	43	2.5	112−	0.89
3	42	2.3	117+	.85
4	39	1.8	108−	.93
5	39	1.8	108−	.93
6	45	2.7	123+	.81
7	46	2.8	128+	.78
8	48	3.4	133+	.75
9	39	1.8	113+	.88
10	47	3.3	119−	.84
Mean	43	2.5	115	.87

Probable error of a single observation.............8 min.
Percentage error of a single observation............7%
Probable error of the mean........................2.4 min.
Percentage error of the mean......................2.1%

[a] Estimated from length. [b] Minus sign means fish was dead when taken out; plus sign means that fish was not quite dead, as shown by reaction to hydrochloric acid.

The condensed results of the complete series of tests is shown in Table II, with those of a statistical study of the method.

In this table the probable errors are calculated from the approximate equations

$$r = 0.8453 \frac{\Sigma v}{\sqrt{n(n-1)}} \text{ and } r_0 = 0.8453 \frac{\Sigma v}{n\sqrt{n-1}}.$$

In these equations r is probable error of a single observation; r_0 is probable error of the arithmetic mean; v is residual (difference between observed survival time and arithmetic mean); v is sum of individual residuals; n is number of observed survival times. These statistical data show that, although the percentage error of a single observation at points on the critical portion of the curve (that is, the portion approximating an equilateral hyperbola) may be as high as 20%, by using ten or twelve fishes the percentage error of the mean may be lowered to 7% or better. The same procedure used with compounds other than rotenone also gave a percentage error of the mean of 7%.

Table II

Toxicity of Rotenone to Goldfish at 27.0±0.2°

Concn. mg. per liter	No. of fishes used	Mean length of fishes, mm.	Mean weight of fishes,[a] g.	Mean surv. time, min.	Mean $\frac{100}{\text{surv. time}}$	Probable error		Percentage error	
						Of a single observ., min.	Of mean, min.	Of a single observ.	Of mean min.
4.0	4	40	2.0	46	2.19	...	...	..	...
3.0	3	37	1.6	46	2.16	...	...	..	...
2.0	4	37	1.6	48	2.08	...	...	..	...
1.0	4	39	1.8	49	2.06	...	...	..	...
0.90	7	38	1.7	52	1.91	...	...	..	...
.70	7	39	1.8	60	1.71	8	2.8	13	4.7
.50	8	39	1.8	57	1.82	8	2.5	14	4.5
.30	13	39	1.8	70	1.51	13	3.7	19	5.3
.20	16	38	1.7	65	1.55	5	1.2	7	1.8
.10	12	42	2.3	95	1.08	21	5.9	22	6.2
.075	10	43	2.4	115	0.87	8	2.4	7	2.1
.050	11	41	2.2	150	.70	27	8.2	19	5.7
.035	12	41	2.2	252	.42	51	14.8	20	5.9
.025	16	43	2.4	589	.23	244	61	41	10.3
.015	7	..	...	2400	.04	756	288	32	12.0

[a] Estimated from length.

The survival time curve and the velocity of fatality curve are plotted in Fig. 1. In the former the ordinates are survival times in minutes; in the latter the ordinates are the reciprocals of the survival times multiplied by 100 to avoid decimals; in both curves the abscissas are concentrations. It is apparent that data falling outside of the critical portions of the curves are useless in a study of comparative toxicity. Along that portion of the

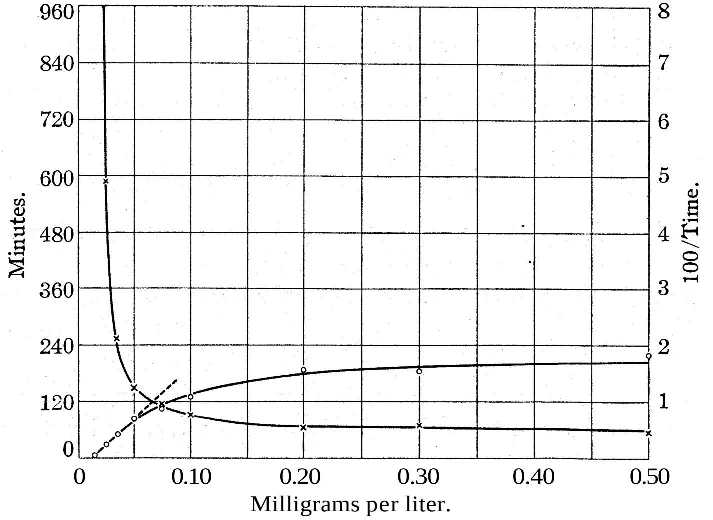

Fig. 1.—Curves showing toxicity of rotenone to goldfish.

survival time curve which approaches the horizontal, great differences in concentrations correspond to comparatively small differences in survival times, whereas along that portion of the curve which approaches the perpendicular, very small differences in concentrations correspond to great differences in survival times. These curves are similar to those obtained by Powers except that in the case of rotenone the initial slow increase in the velocity of fatality with increase in concentration was not found. This may be due to the great toxicity of rotenone.

The value for rotenone obtained from the accompanying velocity of fatality curve by using the formula $\sqrt{\tan \Theta/a}$ is 4 units of toxicity; those for phenol and potassium cyanide, calculated from the curves given by Powers, are 0.0008 and 0.16 unit, respectively. These values are not entirely comparable, since that for rotenone is obtained at 27° and those for potassium cyanide and phenol at 21.5°, but it is apparent that according to this formula rotenone is more toxic to goldfishes than is potassium cyanide, and the latter is 200 times as toxic as phenol.

Conclusions

The method described in this paper is suitable for the study of toxicity. The goldfishes should be as uniform in size as possible; they should not be even slightly out of condition. The tests should be carried out at a constant temperature. Ten or twelve fishes should be used at each concentration; the use of this number lowers the percentage error of the mean to 7% or less with the exception of long survival times (over five hours). The most suitable criterion is the death point. The death point is not so easily recognized with precision as is claimed by Pittenger,[4] but may be determined with fair accuracy as described in the foregoing method. A series of tests at various concentrations should be made in order that survival time curves and velocity of fatality curves may be plotted. Data falling outside that portion of the former curve which approximates an equilateral hyperbola are useless for a study of comparative toxicity. If substances are compared by the single survival time method, this survival time should fall on that critical portion of the curve.

WASHINGTON, D. C.

[CONTRIBUTION NO. 97, CARBOHYDRATE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

SAGITTOL. A NEW SESQUITERPENE ALCOHOL

BY E. YANOVSKY

RECEIVED MAY 31, 1930 PUBLISHED AUGUST 5, 1930

During the course of a systematic investigation of the carbohydrates of a number of uncultivated plants which are indigenous in the United States, attention was directed to *Balsamorrhiza sagittata* (Pursh) Nutt because of the peculiarly pleasant camphor-like odor of its roots and the fact that it and related species (B. helianthoides, B. *deltoidea*, etc.), have been used medicinally and for food purposes by the Indians of the Northwest.[1]

B. sagittata is a low plant, 12 to 18 inches high, with yellow flowers similar to the sunflower, and grows abundantly in Montana, Idaho, Oregon, Utah and Nevada.[2]

The root was eaten by the Indians only after peeling off the cortex which, according to Havard,[1] contains a "terebinthine balsam." Search of the literature has revealed no record of an investigation of this substance.

Upon distilling the roots with steam a crystalline substance separated from the distillate as fine, white needles, the yield being a little less than 0.5% based on the weight of the dry cortex. One recrystallization from alcohol was sufficient for purification, and the substance obtained was quite soluble in alcohol, ether and benzene. It has a pleasant odor, distinctly resembling that of camphor.

G. L. Keenan, of the Food, Drug and Insecticide Administration, has kindly furnished me with the following description of the crystals.

> "This substance crystallizes in very fine needles which are soluble in the organic liquids commonly used in the immersion method but are insoluble in solutions of potassium mercuric iodide in glycerol and water. The needles were found to have a negative elongation, that is, to exhibit their lowest index of refraction lengthwise. The extinction is parallel. The lowest value which it is possible to find is n_D **1.520, and this** may be taken as α for the substance. A higher value, n_D **1.540,** is shown on the needles crosswise and may be considered as γ for the substance."

The melting point of the pure substance is 77–78° (uncorr.). The specific rotation, determined in 95% alcohol solution, is $[\alpha]^{20}_{D}$ + 25.8° for C = 2.080, and +26.5° for C = 2.424 g. per 100 cc. Combustion analyses gave the following results.[3]

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[1] Report Commiss. of Agr. for **1870,** p. **404; J. Lindley** and **T.** Moore, "The Treasury of Botany," **1870,** Vol. I, p. **120;** V. Havard, *Bull. Torrey Bot.* **Club, 22, 98** (1895); F. V. Coville, Contrib. U. S. Nat. Herbar., 5, **62 (1897); J. W.** Blankinship, Mont. Agr. Coll. Expt. Sta. Bull. No. **56 (1905);** R. V. Chamberlin, *Proc. Acad. Nat. Sci. Phila.,* **63, 24 (1911);** G. B. Grinnell, "The Cheyenne Indians," **1923,** Vol. II, pp. **166–191;** J. **R.** Anderson, "Trees and Shrubs of British Columbia," Victoria, B. C., **1925.**

[2] Grateful acknowledgment is made of the courtesy of R. H. Rutledge, District Forester, U. S. Forest Service, Ogden, Utah, in furnishing a supply of roots.

[3] These and subsequent combustion analyses were performed by E. K. Nelson of this Bureau, to whom I am also grateful for general interest in this work.

(1) Subs., 0.0538: H_2O, 0.0560; CO_2, 0.1604; H, 11.65; C, 81.33
(2) Subs., 0.0709: H_2O, 0.0741; CO_2, 0.2101; H, 11.69; C, 80.85
(3) Subs., 0.0779: H_2O, 0.0827; CO_2, 0.2314; H, 11.88; C, 81.03
(4) Subs., 0.0727: H_2O, 0.0766; CO_2, 0.2155; H, 11.79; C, 80.86

Average values: H, 11.75; C, 81.02. Calcd. for $C_{15}H_{26}O$: H, 11.79; C, 81.01; 0, 7.20.

The molecular weight of the substance was determined by the depression of the freezing point (Beckmann's method), benzene being used as a solvent. Two determinations resulted in values for the molecular weight of 220 and 224. The molecular weight was also determined by Rast's method:[4] 0.012 g. of substance in 0.112 g. of camphor caused a 20° depression in the melting point. Several determinations gave an average molecular weight of 214. The calculated molecular weight for the compound $C_{15}H_{26}O$ is 222.

Having established the empirical formula, the nature of the oxygen atom was determined by acetylation. Two grams of the substance was gently boiled with 5 cc. of acetic anhydride and a little fused sodium acetate for about an hour on a sand-bath. The resulting liquid was then poured into water, where it separated as a sirup but did not crystallize on standing. After being washed several times with water, the sirup was dissolved in ether, dried with anhydrous sodium sulfate, and the solvent evaporated in *vacuo*. It was again dissolved in alcohol and the solvent evaporated. After being thoroughly dried in a vacuum desiccator over both sodium hydroxide and calcium chloride, the sirup was analyzed with the following results.

(1) Subs., 0.0866: H_2O, 0.0819; CO_2, 0.2446; H, 10.58; C, 77.05
(2) Subs., 0.0908: H_2O, 0.0868; CO_2, 0.2572; H, 10.70; C, 77.27

Average values: H, 10.64; C, 77.16. Calcd. for $C_{15}H_{25}OCOCH_3$: H, 10.68; C, 77.21; 0, 12.11.

The compound, which we have named "sagittol," is therefore a sesquiterpene alcohol. It is not identical in properties with any of the sesquiterpene alcohols described in the literature. Upon standing in a desiccator for several months sagittol became somewhat sticky and upon attempted recrystallization yielded a sirup instead of crystals. This compound will be investigated further as soon as additional plant material is available.

Summary

A new compound named "sagittol" has been isolated from *Balsamorrhiza sagittata* (Pursh) Nutt, and some of its properties determined.

From combustion and molecular weight determinations, the compound was found to have a molecular weight of 222, with the empirical formula $C_{15}H_{26}O$. The compound contains an alcohol group and is, therefore, a sesquiterpene alcohol.

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[4] Rast, **Ber.,** 55, 1051 (1922).

The melting point of sagittol is 77–78' (uncorr.); its average specific rotation in 95% alcohol is +26.15° at an average concentration of of 2.252 g. per 100 cc. Sagittol crystallizes as very fine needles, the optical properties of which have been determined.

WASHINGTON, D. C.

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES.

XXXI. THE BEHAVIOR OF CELLULOSE TOWARD SOLUTIONS OF ALUMINUM SALTS

BY EDMUND G. V. PERCIVAL,[1] A. C. CUTHBERTSON[1] AND HAROLD HIBBERT

RECEIVED JUNE 5, 1930 PUBLISHED AUGUST 5, 1930

In view of the important role played by aluminum sulfate in the process of the rosin sizing of paper, many investigations have been carried out to ascertain the mechanism of the adsorption by the cellulose fiber. Schwalbe and Robsahm,[2] using sulfite pulps, claimed that cellulose decomposed aluminum sulfate up to 3% of its weight, but Schwalbe[3] in a re-investigation of the problem states that neither cotton nor pulp takes up appreciable amounts of aluminum hydroxide from aluminum sulfate solutions. Sutermeister[4] found that the amount adsorbed was never greater than 0.3% of the weight of the fiber and was independent of the concentration of the aluminum sulfate solution employed.

It was concluded by Tingle[5] that the observed withdrawal of aluminum hydroxide from solutions of aluminum sulfate in the presence of cellulose is due to the non-cellulosic constituents of the fiber. He could detect no adsorption by ordinary analytical methods where the cellulose was of a reasonable degree of purity, and concluded that within the limits imposed pure cellulose will adsorb no aluminum hydroxide from the solution.

In the case of aluminum acetate, and also in some cases with aluminum sulfate, Haller[6] found "negative adsorptions" by analysis of the residual solutions, but actually in every case, some fixation of aluminum hydroxide by the fiber had occurred. Durst[7] also found that "negative adsorption" took place with wood pulps from aluminum acetate solutions. The ash

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[1] Research Fellow, Pulp and Paper Research Institute, Montreal, Canada. The authors desire to express their thanks to the Canadian Pulp and Paper Association for financial assistance rendered in connection with this investigation.

[2] Schwalbe and Robsahm, *Wochenblatt,* 43, 1454 (1912).

[3] Schwalbe, *Z. angew. Chem., 37,* 125 (1924).

[4] Sutermeister, *Pulp and Paper Mag. of Canada, 11,* 803 (1922).

[5] Tingle, *J. Ind. Eng. Chem., 14,* 198 (1922).

[6] Haller, *Chem.-Ztg.,* 42, 597 (1918).

[7] Durst, *ibid.,* 43, 373 (1919).

content of the original pulp however, decreased, although aluminum was present in the ash after adsorption.

This so-called negative adsorption appears to be due partly to adsorption of water by the fiber[8] and partly to the entry into solution of the mineral constituents of the ash of the pulp.

Michaelis and Rona,[9] using the salts of basic and acid dyes with cellulose, first advanced the theory of "Exchange Adsorption" which has been applied to the case of aluminum sulfate and cellulose by Roschier[10] and by Kolthoff.[11]

According to the latter investigator, the ash is supposed to act as a type of calcium permutite, exchanging aluminum for calcium thus

$$3\text{Ca-permutite} + 2\text{Al}^{+++} \rightleftharpoons 2\text{Al-(permutite)}_3 + 3\text{Ca}^{++}$$

The purpose of this investigation was to determine (a) whether "ash-free cellulose" adsorbs aluminum compounds from solutions of aluminum salts; (b) the hydrolysis of the aluminum salts in solution and the effect of this factor on the adsorption; (c) the nature of the "Exchange Adsorption."

Preparation of Materials.—The aluminum sulfate, obtained from Merck and Co. gave an analysis Al_2O_3, 16.64%; SO_3, 39.00%. Solution in water left a small amount of insoluble residue amounting to 0.15%. The clear solution obtained on filtering gave a ratio of $Al_2O_3:SO_3 = 1:3.001$. The material was taken therefore as a representative sample of normal aluminum sulfate.

Owing to the difficulty of obtaining either pure aluminum acetate or chloride, these were prepared from the normal aluminum sulfate solution and the corresponding barium salt. Equivalent solutions were mixed and the precipitated barium sulfate was removed by centrifuging. The solution was then adjusted until no precipitate was obtained on the addition of either component.

Owing to their instability the aluminum acetate solutions were kept at 0° when not in use.

The celluloses used were

A. Cotton cellulose, a-content, 99.1%; ash, 0.05%.
B. "Brown" a pulp (i), a-content, 95.3%; ash, 0.14%.
C. Whatman Ashless Filter Paper, No. **42**, a content, 99.8%; ash, 0.01%.
D. "Brown" a pulp (ii), a-content, 95.0%; ash, 0.08%.

The ash in each case contained calcium, iron and silica except C, which contained no iron.

The solutions employed for adsorption were shown to be free from calcium, iron and zinc.

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[8] Percival, Cuthbertson and Hibbert, THIS JOURNAL, 52,3257 (1930).

[9] Michaelis and Rona, *Biochem. Z.*, **97**, **57** (1919).

[10] Roschier, *Papierfabrikant*, 49, 757 (1928).

[11] Kolthoff, *Pharm. Weekblad*, 58, 233 (1921).

Experimental

The Adsorption from Aluminum Salt Solutions.—The adsorption was carried out at 25.0° in a glass vessel closed with a firmly fitting glass cap to prevent evaporation.

Three hundred and fifty cc. of each of the respective solutions was used for each experiment and 20 g. of air dry cellulose, or pulp, which was shaken up well with the solution and allowed to stand in the thermostat for about twelve hours.

At the end of this time the liquid was filtered off and the cellulose washed with 2000 cc. of distilled water three times in succession, making a total of six liters, the operation extending over one hour. The material was then dried for a few minutes at the pump, transferred to a beaker and 50 cc. of strong hydrochloric acid (d, 1.18) was added, the mixture then being allowed to stand at room temperature for two hours. The acid was filtered off and the cellulose thoroughly washed with 800 cc. of water, the filtrate and washings being collected and evaporated to 100 cc. Ammonium chloride was added to the latter and the mixture boiled. This was followed by the addition of ammonium hydroxide to precipitate aluminum hydroxide which was collected, ignited and weighed as Al_2O_3.

Analysis of the ash of the cotton or pulp after the adsorption and acid treatment failed to reveal the presence of alumina, indicating the efficiency of the process for removing adsorbed aluminum hydroxide.

Effect of Dilution and Hydrogen-Ion Concentration on the Adsorption from Aluminum Sulfate Solutions.—The hydrogen-ion concentration measurements were made using a Leeds and Northrup potentiometer in conjunction with a calomel half cell and a hydrogen electrode.

The effect of dilution (and the corresponding change of P_H) on the adsorption was studied with respect to cotton cellulose "A."

The results are given in Table I; v represents dilution in liters per gram molecule and the adsorptions are expressed in grams of Al_2O_3 per 100 g. of cellulosic material. Throughout this paper they will be designated as N.

TABLE I

EXPERIMENTS WITH SURGICAL COTTON (SAMPLE A). EFFECT OF VARIATION IN CONCENTRATION OF ALUMINUM SULFATE SOLUTIONS

v	P_H	N
4.86	2.84	0.050
16 91	3.09	.053
18 06	3.13	.060
50.20	3.24	.062
84.50	3.33	.080
340.20	3.54	.072

It is evident that the adsorption increases slightly with increasing dilution.

The influence of hydrogen-ion concentration was studied on celluloses C and D ("Brown" α pulp and Whatman's ashless filter paper).

The change in P_H was accomplished by the appropriate addition of carbonate-free sodium hydroxide solution. The slight precipitate which formed in the preparation of the solutions for Expts. 3 and 4, Table II, was filtered off and the clear solution used in the adsorption experiments.

It is evident that a change in P_H value brings about a marked alteration in the adsorption.

Since an analysis of each of the equilibrium solutions indicated the presence of calcium and iron in appreciable amounts, the question naturally arose as to whether the entire adsorption was due to this factor.

TABLE II

EXPERIMENTS ON THE EFFECT OF VARIATION IN HYDROGEN-ION CONCENTRATION OF ALUMINUM SULFATE SOLUTIONS

No.	v	P_H	Brown a pulp (D)	Whatman's ashless filter paper
1	50.2	3.24	0.054	0.020
2	49.4	3.65	.060	.031
3	49.5	3.83	.082	.033
4	53.9	3.83	.081	.035

It was also of interest to determine whether all of the constituents originally present in the ash passed into solution during a single adsorption, or were progressively removed in decreasing amounts upon a repetition of the first treatment.

Successive Adsorption Experiments in Solutions of Aluminum Sulfate.—Successive adsorption experiments were carried out in the following manner. The actual experimental method was exactly the same as previously described for a single adsorption. After removal of the hydrochloric acid extract, the cellulose sample was washed repeatedly, using a total volume of four liters of water, then dried at the pump and the adsorption process repeated.

The results are given in Table III for an aluminum sulfate solution, v, 51.2; P_H, 3.25.

TABLE III

RESULTS

Adsorption..................	No. 1	No. 2	No. 3	No. 4
% Adsorption per 100 g. N (B')	0.070	0.023	0.018	0.010
% Adsorption per 100 g. N (C')	.020	.011	.007	.005

With both cellulose products, calcium, and in the case of cellulose B, iron, was found in the solution after the first adsorption, but apparently very little in the subsequent treatments.

The treatment of the cellulose with hydrochloric acid solution (about 25% HCl after dilution with the water in the pulp) results in a small amount of degradation as shown below.

Alpha-cellulose determinations were made using a slight modification of the American Chemical Society method[12] on the pulp "B" after adsorption from aluminum sulfate solution and treatment with hydrochloric acid; this gave an indication of the extent to which this degradation had taken place.

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[12] Moore, M.Sc. Thesis, McGill University, May, 1930.

The a-cellulose values after successive adsorptions and acid treatment are given in Table IV.

TABLE IV

or-CELLULOSE VALUES

Adsorptions	No 0	No 1	No 2	No 3	No. 4
Alpha-cellulose value	95 3	92 1	90 8	..	88 2

The "successive adsorption" method of attack was extended to aluminum acetate and chloride solutions, to find how the increased degree of hydrolysis and the specific nature of the anion would alter the amount of aluminum hydroxide taken up. The results are given in tables V and VI

TABLE V

EXPERIMENTS WITH ALUMINUM ACETATE SOLUTIONS

v, 49.7; PH, 4.41

Adsorption	No 1	No 2	No 3	No 4
% Adsorption (N) Sample B	0.119	0.084	0.063	0059
% Adsorption (N) Sample C	.051	,042	,039	.034

A trace of calcium was still found in the residual liquid after the third adsorption using Sample B.

TABLE VI

EXPERIMENTS WITH ALUMINUM CHLORIDE

v, 49.1; *PH*, 2.97

Adsorption	No 1	No. 2	No. 3	No. 4
% Adsorption (N) Sample B	0.065	0 047	0.029	0.024
% Adsorption (*N*) Sample C	.024	.018	.014	.014

Qualitatively, calcium appeared to be removed as slowly as in the case of aluminum acetate.

Discussion of Results

A consideration of Table I leads to the conclusion that a slight increase in adsorption of aluminum hydroxide takes place with dilution, involving a correspondingly smaller hydrogen-ion concentration. The same effect is apparent in Table II, where dilution is practically constant and hydrogen-ion concentration decreases in approximately the same way.

It would appear therefore that in addition to exchange adsorption, at least part of the latter is to be attributed to the removal of $Al(OH)_3$ from the solution, formed by hydrolysis of the aluminum sulfate.

Tables III, V and VI represent successive adsorption experiments from solutions of the sulfate, acetate and chloride, respectively.

It is to be noted that the difference between the first and second adsorption values in Table III is very marked as compared with corresponding values in Tables V and VI.

Since, as indicated above, a large part of the calcium and iron is removed after the first adsorption from aluminum sulfate solution, while the removal. is much slower in the other two cases, it would appear logical to assume that adsorption is closely associated with the calcium and iron content of the ash.

Inasmuch as a slight amount of degradation arises from the action of the hydrochloric acid which is used to remove the aluminum hydroxide, the validity of the successive adsorptions might be considered as depending on the extent to which this degradation takes place.

However, Freundlich[13] has shown that the adsorption by a pure cellulose is much less than for a cellulose which has been subjected to drastic chemical treatment. Also Clibbens and Ridge,[14] in studying the rate of oxycellulose formation, show that the greater adsorption of methylene blue occurs at the point of maximum degradation.

From this evidence, therefore, one would anticipate an increased adsorption by the cellulose with an increasing number of treatments with hydrochloric acid.

If the decreasing values found for successive adsorptions cannot be attributed to a degradation of the fiber it would seem that the conclusion is permissible that the amounts of aluminum hydroxide taken up by the fiber depend on two factors (i) a "natural" and (ii) an "exchange" adsorption.

The "natural" adsorption is a variable quantity possibly depending on the specific nature of the fiber, the extent of hydrolysis of the solution, the hydrogen-ion concentration and the anion; under normal conditions it plays a minor role in comparison with that of the "exchange" adsorption.

According to Michaelis and Rona[g] and Kolthoff,[11] the "exchange" adsorption depends on the replaceable elements in the ash.

If it is comparable to the case of the permutite the "exchange" adsorption must be a fixed amount depending only on the ash constituents.

A consideration of Table III for aluminum sulfate shows that the first adsorption may be made up of a relatively high "exchange" value and a small "natural" adsorption. Since nearly all of the calcium and iron is removed in the first treatment, the successive values are much lower, and the fourth value is presumed to correspond to the "natural" adsorption of a cellulose free from replaceable ash constituents under those conditions. In the case of the other salts of aluminum the removal of these replaceable constituents is much slower (Tables V and VI), as evidenced by the gradual decrease of the values of *N*, which is further substantiated by the experimental fact that a definite amount of calcium was present even after the second treatment.

Assuming the "exchange" adsorption to be a property of the aluminum ion, and having the same value for each of the three different aluminum solutions used, the "exchange" value can be calculated in the case of the sulfate, and applied to the other salt solutions to calculate the "natural"

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[13] Freundlich, *Cellulosechemie,* 7, 57 *(1926).*

[14] Clibbens and Ridge, *Shirley Inst. Mem., VI, 1 (1927).*

adsorptions. These values thus calculated are shown to agree with the value of N at the fourth adsorption (selected as the natural adsorption in the case of aluminum sulfate), and this is taken as the mean "natural" value.

The calculation is carried out in the following way. From Table III each of the first three adsorptions represents "exchange" combined with "natural" adsorption. Natural adsorption for cellulose B = 0.010 and this amount of aluminum hydroxide (expressed as Al_2O_3) is adsorbed in each case as well as the amount contributed by the exchange process.

Hence total "exchange" adsorption for cellulose B $= 0.070 + 0.023 + 0.018 - 3 \times 0.010 = 0.081$, and for cellulose C $= 0.020 + 0.011 + 0.007 - 3 \times 0.005 = 0.023$.

Taking these values as fixed, the mean "natural" adsorption from the results contained in Table V for aluminum acetate is calculated thus

$$\text{Total adsorption} = 0.119 + 0.084 + 0.063 + 0.059 = 0.325$$
$$\text{Exchange adsorption from above} = 0.081$$
$$\text{Therefore mean natural adsorption} = \frac{0.325 - 0.081}{4} = 0.061$$

A comparison of the observed (value at fourth adsorption) and calculated "natural" adsorptions, is given in Table VII.

TABLE VII

COMPARISON

			% Adsorp., sample B		% Adsorp., sample C	
Salt	v	PH	Observed	Calculated	Observed	Calculated
$Al_2(SO_4)_3$	51.2	3.25	0.010	..	0.005	..
$Al(C_2H_3O_2)_3$	49.3	4.41	.059	0.061	.034	0.036
$AlCl_3$	49.1	2.97	.024	.021	.014	.012

The values agree very closely and it would seem therefore that "exchange" adsorption ceases after four adsorptions.

The "natural" adsorptions from solutions of aluminum acetate and chloride are much greater than from the sulfate solutions. This is to be anticipated since the hydrolysis is more marked in the former solutions.

Denham[15] and Pelling[16] by electrometric methods determined the extent and mechanism of the hydrolysis of aqueous aluminum sulfate and chloride solutions, and showed that the chloride suffered greater hydrolysis than the sulfate under identical conditions, and that a single water molecule was most probably concerned in effecting the hydrolysis, *e. g.*, $AlCl_3 + H_2O \rightleftharpoons Al(OH)Cl_2 + HCl$.

In order to complete the comparison, the hydrolysis of aluminum acetate was studied using a similar technique. The results are given in Table VIII.

Comparison with the results of Denham[15] and Pelling[16] shows that of the three salts the acetate undergoes most hydrolysis. Furthermore, the

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[15] Denham, *J.* Chem. *Soc.*, 99, 41 (1908).

[16] Pelling, *J. Chem.* Met, *Min. Soc. South Africa*, **26**, 88 **(1925).**

hydrolysis constant K corresponds most closely with the same mechanism as assumed for the other two aluminum salts

$$Al(C_2H_3O_2)_3 + H_2O \rightleftharpoons AlOH(C_2H_3O_2)_2 + C_2H_4O_2$$

TABLE VIII

HYDROLYSIS OF ALUMINUM ACETATE AT 25°

v	$C_H \times 10^4$	$100\ x$	$K \times 10^4$
7.64	0.589	3.77	1.94
15.28	.513	4.75	1.55
31.56	.447	5.99	1.21
49.70	.389	6.64	0.95
63.12	.389	7.43	.95
126.20	.347	9.41	.78
252.5	.347	13.45	.83

$100\ x$ = percentage hydrolysis.

$K = X^2/(1-x)v$, for the first stage hydrolysis.

Ostwald's dilution law was used to calculate the value of C_H and the ionization constant for acetic acid was taken to be 1.8×10^{-5} at 25°.

It is evident therefore, that since the three salts undergo the same type of hydrolysis, the natural adsorption is connected, for the most part, with the extent to which the equilibrium

$$AlX_3 + H_2O \rightleftharpoons Al(OH)X_2 + HX$$

is shifted to the right, concomitant with the change in hydrogen-ion concentration.

Whether aluminum hydroxide is taken up directly from the solution by the fiber as suggested by Bancroft[17] or whether the basic aluminum salts known to be present are first adsorbed and then decomposed by adsorbed water, is not clear.

The fact remains however that except in strongly hydrolyzed solutions, such as aluminum acetate, by far the major part of the adsorption is due to the exchange process between iron and calcium (presumably as silicate) and the aluminum salts.

The conclusions to be drawn are that with solutions of these three salts of aluminum, the adsorption by cellulose may be represented by a small "natural" adsorption on which an "exchange" adsorption is superimposed, the mechanism of the latter being comparable to the permutite theory as advanced by Kolthoff.

Summary

1. The adsorption from aluminum salt solutions by different celluloses has been studied and by successive adsorption experiments it has been shown that small but definite amounts of $Al(OH)_3$ are adsorbed by ash-free cellulose, *i. e.*, a cellulose free from constituents capable of "exchange."

2. The adsorption has been found to be made up of two effects, the

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[17] Bancroft, *J. Phys. Chem.*, 26, 501 (1922).

"natural" adsorption and the "exchange" adsorption. The "natural" adsorption depends on the dilution and P_H value of the solution. The "exchange" adsorption seems to depend on the mineral content of the original ash, principally on the amounts of calcium and iron present.

3. The mechanism of the hydrolysis of aluminum acetate is shown to be the same as for the chloride and sulfate solutions, while the adsorption increases with increasing hydrolysis, being highest for the acetate.

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[CONTRIBUTION NO. 66 FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

RING ENLARGEMENT WITH DIAZOMETHANE IN THE HYDROAROMATIC SERIES[1]

BY ERICH MOSETTIG AND ALFRED BURGER

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The present investigation was begun in a search for a preparative way to amino-alcohols of the type V, since compounds of this class may be expected to have interesting pharmacological properties. The oxide III appears to be the most convenient starting point for the synthesis of such substances; by simple addition of primary and secondary amines, with opening of the ethylene oxide ring, the oxide must be converted to amino-alcohols of the desired type. A method for the preparation of this hitherto unknown oxide lies in the action of diazomethane on cyclohexanone; the expected oxide represents, however, but one phase of the reaction.

The action of diazomethane on the carbonyl group in the aliphatic, aromatic, and heterocyclic series has been the subject of numerous recent investigations. Arndt and his co-workers[2] were the first to show that the reaction discovered by H. Meyer[3] and Schlotterbeck,[4] in which aldehydes are converted to the corresponding ketones by the action of diazomethane

$$\mathrm{RCHO} \xrightarrow{\mathrm{CH_2N_2}} \mathrm{RCOCH_3}$$

is not of general application. In some cases the reaction leads to the isomeric ethylene oxide derivative, while the ketone and a homolog are formed in small amounts as by-products. The mechanism postulated

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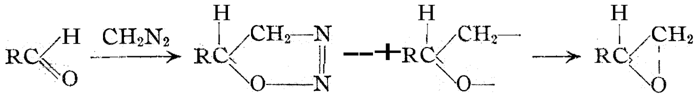
[1] This work was supported by funds from the Committee on Drug Addiction of the National Research Council.

[2] Arndt and Partale, *Ber.*, 60,446 (1927); Arndt, *Z. angew. Chem.*, 40,1099 (1927); Arndt and Eistert, *Ber.*, 61, 1118 (1928); cf. Amdt, Eistert, and Amende, *ibid.*, 61, 1952 (1928); Arndt, Eistert, and Ender, *ibid.*, 62, 44 (1929).

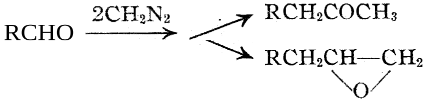
[3] H. Meyer, Monatsh., 26,1300 (1905); *Ber.*, 40, 847 (1907).

[4] Schlotterbeck, *ibid.*, 40,479 (1907); 42, 2559 (1909).

by these authors, which also accounts for the occurrence of the by-products, expresses the formation of the oxide by the equation

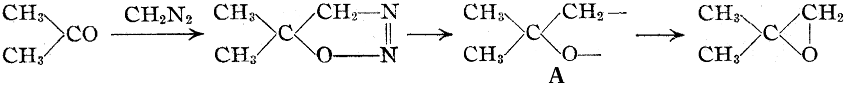


Mosettig[5] in an independent investigation of a special case—that of piperonal—obtained results differing from those of Arndt; from this aldehyde the chief products were substances which must have been formed by introduction of two CH_2 groups into the aldehyde

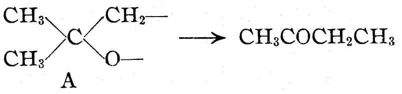


These results may easily be explained according to the Arndt mechanism; in this connection the influence of the methyl alcohol added to the reaction mixture has been emphasized.[6]

Meerwein and Burneleit[7] investigated at about the same time the action of diazomethane on acetone. Acetone alone is indifferent toward diazomethane, but reacts in the presence of catalysts, as water, alcohols or metal salts, to form asymmetric dimethyl ethylene oxide as the chief product, together with methyl ethyl ketone, and probably methyl *n*-propyl ketone and diethyl ketone. These authors formulated the reaction as proceeding to the oxide in the way already expressed by Arndt for aldehydes, in the equation


(1)

and postulated further that, through wandering of a CH_3 group in the hypothetical intermediate A, methyl ethyl ketone is formed


(2)

This ketone then reacts further with diazomethane to form in an analogous way the higher ketones, which were shown to be probably present.

Cyclohexanone, in ethereal solution, is practically indifferent toward diazomethane. When methyl alcohol is added, a rather vigorous reaction, with nitrogen evolution, begins. We were able to isolate as products cycloheptanone (suberone), cyclo-octanone (azelaone) and an oxide (III), isomeric with cycloheptanone. The chief product is cycloheptanone, while

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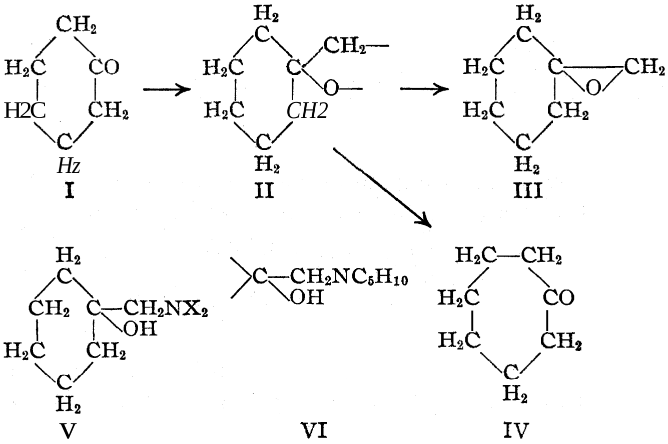
[5] Mosettig, Ber., 61, 1391 (1928); 62, 1271 (1929).

[6] Cf. Mosettig and Jovanovič, *Monatsh.*, 53 and 54, 430, footnote 6 (1929).

[7] Meerwein and Burneleit, Ber., **61**, 1840 (1928). Cf. Meerwein, Bersin and Burneleit, *ibid.*, 62, 999 (1929).

cyclo-octanone and the oxide in nearly equal amounts represent by-products. Following the Arndt–Meerwein scheme, the process may be represented



The conversion of II to III takes place parallel to that in Equation 1 for acetone, II to IV as in Equation 2; a ring CH_2 group adjacent to the carbonyl wanders to the open methylene group, which in this case must lead to expansion of the ring.[8] The transformation of cycloheptanone into cyclo-octanone takes place in an analogous way.

In order to exclude any possibility of error, the cyclohexanone employed was purified through the bisulfite compound and semicarbazone. The reaction products were separated by treating the ethereal solution with sodium bisulfite, which removed cycloheptanone. The cyclo-octanone, which forms no bisulfite compound: could be separated from the oxide III in two ways: by precipitation as the semicarbazone, or by treating the mixture with piperidine, and making use of the basic properties of the resulting piperidino alcohol to separate it from the cyclo-octanone, which is obviously indifferent to piperidine under the conditions of the experiment.

The cycloheptanone was characterized as semicarbazone and dibenzylidene compound, which were compared by mixed melting point with the same derivatives of cycloheptanone from suberic acid.

Cyclo-octanone was likewise identified in the form of its semicarbazone and dibenzylidene compound; the semicarbazone was compared with a

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[8] Ring expansion with diazomethane was observed for the first time by Heller [*Ber.*, 52, 741 (1919); 59, 704 (1926)] in the change of isatin to dihydroxyquinoline. Arndt [Arndt, Eistert and Ender, *ibid.*, **62**, 44 (1929)], in the course of his investigations, revised and clarified the Heller formulation, in the light of his work. Very recently Hantzsch and Czapp have reported the conversion of oxindone-carboxylic ester into 1-hydroxy-4-methoxynaphthaline-2-carboxylicester [*ibid.*, 63, 566 (1930)]. *Cf.* Arndt, *ibid.*, 63,1180 (1930).

[9] Ruzicka and Brugger, *Helv. Chim. Acta*, 9,339 (1926).

sample of cyclo-octanone semicarbazone generously supplied by Professor Ruzicka, with which it showed no depression in mixed melting point.

The oxide III was isomerized by distillation at atmospheric pressure over a trace of zinc chloride to hexahydrobenzaldehyde, which was characterized as the semicarbazone. This semicarbazone proved to be identical (mixed melting point) with the semicarbazone of hexahydrobenzaldehyde prepared according to Kon[10] from cyclohexylmagnesium chloride and ethyl orthoformate.

The oxide was also converted to a piperidino alcohol, which probably has the structure VI, assuming that the addition of the amine takes place in accordance with the general rule for addition of ammonia or amines to asymmetric ethylene oxides, the hydroxyl being formed on the carbon carrying the least hydrogen.

It is not excluded that the oxide III may have undergone some change, as isomerization, hydration or polymerization during the bisulfite treatment; this method of separation seemed, however, the most practicable. The cycloheptanone results from a primary reaction, as is shown by the simultaneous appearance of cyclo-octanone, which can hardly be explained except as a product of the further reaction of diazomethane on cycloheptanone formed in the original reaction mixture. The starting substance, cyclohexanone, could not be detected in the end-products.

Cyclopentanone was brought into reaction with diazomethane under the same conditions as in the case of cyclohexanone; for convenience in working up the product, an excess of diazomethane was used. The products of the completed reaction were worked up in the same manner as for the cyclohexanone reaction; cycloheptanone was found to be the chief product; cyclo-octanone was formed in smaller amount. Isomerization of the oxide fraction resulted in an aldehyde-containing distillate (fuchsin–sulfurous acid test) but separation of the mixture of semicarbazones (probably of cyclopentane aldehyde and hexahydrobenzaldehyde) failed. No crystalline products could be obtained from the action of piperidine. Cyclopentanone and cyclohexanone could not be detected.

The ring expansion described in this paper brings a new proof of the validity of the Meerwein assumption of radical wandering in the hypothetical intermediate A in Equation 2. It is possible that still higher homologs of the cyclic ketones or oxides are present among the reaction products from cyclopentanone and cyclohexanone. A systematic investigation carried out on large quantities of the homologous cyclic ketones might decide this, and at the same time make important contributions to our knowledge of ring strain and ring widening. A similar study of the action of diazo-ethane and its homologs would also be desirable in this connection, but lies outside the field of our researches.

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[10] Kon, *J. Chem. Soc.*, **128**, 1797 (1926).

Ketones of hydroaromatic nature which share two carbon atoms with one or more aromatic rings offer better prospects of success for the preparation of oxides of the desired type. We plan therefore to extend our studies of this reaction to tetralon (ketotetrahydronaphthalene) and its analogs.

In consideration of the relatively good yield, ease of preparation and purity of the cycloheptanone and cyclo-octanone obtained in the reaction described, and of the difficulty of the hitherto known preparative methods for these ketones, we believe that the action of diazomethane on cyclohexanone offers a practicable preparative way to these substances.

We take great pleasure in acknowledging our indebtedness to Professor Ruzicka for a sample of cyclo-octanone semicarbazone.

Experimental Part

Cyclohexanone and Diazomethane.—Cyclohexanone was converted into the bisulfite addition compound, and the ketone obtained from decomposition of this with alkali was fractionally distilled. The semicarbazone of the fraction boiling at 157° (corr.) was prepared and recrystallized from methyl alcohol (m. p. 167.5–169°), decomposed with hydrochloric acid, and the cyclohexanone obtained by steam distillation was finally again fractionally distilled.

The diazomethane was prepared from the action of methyl alcoholic potassium hydroxide on nitrosomethylurethan, and titrated with nitrobenzoic acid.

Twenty-four grams of cyclohexanone was added to a solution of 13.6 g. of diazomethane in 900 cc. of dry ether, cooled in ice. No significant evolution of nitrogen took place, even on long standing at 0°; on addition of 200 cc. of absolute methyl alcohol, a vigorous evolution of nitrogen began. When this began to diminish, after several hours, the reaction mixture was removed from the ice-bath, and allowed to stand at room temperature. On the next day the solution was noticeably lighter in color but became completely colorless only after three days. The colorless solution was filtered free of a slight flocculent precipitate (polymethylenes), the ether evaporated and the methyl alcohol removed in vacuum at 22° with a fractionating column. It is here unavoidable that small amounts of volatile substances from the reaction product distil off with the methyl alcohol or ether. For this reason the methyl alcohol was again distilled in vacuum with a fractionating column. The combined distillation residues were dissolved in about 100 cc. of ether and shaken for two to three hours with saturated sodium bisulfite solution. The crystallized bisulfite compound which separated was filtered out and washed many times with ether. The filtrate, consisting of a bisulfite and an ethereal layer, was separated, the bisulfite layer shaken out several times with ether and the ethereal extract combined with the ether layer above mentioned.

The combined ether was washed several times with dilute sodium carbonate solution and dried over sodium sulfate. It contained the oxide and the cyclo-octanone. After evaporation of the ether, the residue was distilled at 20 mm. pressure and the following fractions were collected: Fraction 1, b. p. 35–60°, 2 g.; Fraction 2, b. p. 61–95°, 6.5 g.; Fraction 3, b. p. 95–105°, 2.6 g.

Fraction 1, which consisted chiefly of the oxide, and gave no color with fuchsin–sulfurous acid, was distilled twice at atmospheric pressure over a trace of freshly fused zinc chloride. A drop of the distillate gave with fuchsin–sulfurous acid an intense red-violet color, showing that the isomerization to the aldehyde had taken place. On addition of an aqueous solution of semicarbazide hydrochloride and sodium acetate, a semicarbazone precipitated out immediately; crystallized three times from methyl alcohol, it formed shining leaflets or needles of m. p. 171–172° (sintering at 170°).

Anal, Subs., 4.216 mg.: 0.931 cc. of N (24°, 749 mm.). Calcd, for $C_8H_{15}ON_3$: N, 24.85. Pound: N, 25.01.

To confirm the assumption that this was the semicarbazone of hexahydrobenzaldehyde, hexahydrobenzaldehyde was prepared by the method of Kon[10] from cyclohexylmagnesium chloride and ethyl orthoformate. The semicarbazone of this melted at 172.5–173°, sintering at 171°; the mixed melting point with the semicarbazone of the product from isomerization of the oxide was 171–172°.[11]

Fraction 3 consisted chiefly of cyclo-octanone. It crystallized to a thick paste when cooled in a freezing mixture. It was converted to a semicarbazone in the same manner as Fraction 1, which had the melting point 167.5–169° after one recrystallization from methyl alcohol.

Anal. Subs , 3 586 mg.: 0.739 cc. of N (23°, 744 mm.), 3.680 mg.; CO_2, 7.955 mg ; H_2O, 3.100 mg. Calcd. for $C_9H_{17}ON_3$: C, 58.96; H, 9.36; N, 22.94. Found: C, 58.95; H, 9.43; N, 23.26.

The mixed melting point with Ruzicka's sample of cyclo-octanone semicarbazone of m. p. 168–169° lay at 168–169°.

The colorless dibenzylidene compound of cyclo-octanone, which was obtained in analogy with the Wallach[12] dibenzylidene compound from suberone by condensation with two moles of freshly distilled benzaldehyde in the presence of sodium methylate, melted after recrystallization from slightly diluted methyl alcohol at 107.5–109° (the mixed melting point with the dibenzylidene compound of the same melting point frcm suberone lay at 85–95°).

Anal. Subs., 0.0876: CO_2, 0.2791; H_2O, 0.0572. Calcd. for $C_{22}H_{22}O$: C, 87.37; H, 7.33. Found: C, 86.89; H, 7.31.

Fraction 2 consists apparently of the oxide and cyclo-octanone. Since the small quantity of material put fractional distillation out of consideration, the cyclo-octanone was separated from a sample of the mixture with semicarbazide hydrochloride and sodium acetate. The well-pressed semicarbazone was recrystallized from methyl alcohol and melted at 167–169°. The main portion of Fraction 2 was heated with an equal weight of water and of piperidine in a sealed tube for six hours at 95–100°. The reaction mixture was taken up in ether and water, and the ether layer washed with water to remove most of the unreacted piperidine. The piperidino alcohol was now extracted out of the ether with dilute hydrochloric acid; in the ether remained the unaffected cyclo-octanone, which was characterized as the semicarbazone. The acid layer was made alkaline and extracted with ether. The brown oily residue from evaporation of the ether was freed from piperidine by standing for many days over phosphorus pentoxide in a vacuum desiccator. It was then brought into dry ethereal solution, and the base precipitated as the hydrochloride by addition of ethereal hydrochloric acid. The hydrochloride was dissolved in alcohol and ether added to the point where the solution barely remained clear; on standing, crystals separated, m. p. 194.5–195°.

Anal. Subs., 0.2073: AgCl, 0.1262; 5.476 mg, 0.286 cc. of N (25°, 752 mm.). Calcd. for $C_{12}H_{24}ONCl$: Cl, 15.18; N, 6.00. Found: Cl, 15.06; N, 5.92.

The piperidino alcohol gave no crystalline picrate.

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[11] The melting points of semicarbazones in general depend upon the mode of heating. Perhaps the considerable differences in melting point of this semicarbazone to be found in the literature may be due to this fact. Wallach, *Ann.*, **347**, 333 (1906), m. p. 167–168"; Zelinsky, ***Ber.***, 40, 3051 (1907), m. p. 173–174°; Bouveault, ***Bull. soc. chim.***, [3] 29, 1050 (1903), m. p. 176°; Sircar, ***J. Chem.*** *Soc.*, 55 (1928), m. p. 175"; Danilow and Danilowa, ***Ber.***, 62, 2668 (1929), m. p. 173".

[12] Wallach, *ibid.*, 29, 1600 (1896).

Suberone.—The bisulfite compound separated from the original reaction mixture was combined with the bisulfite mother liquor, made alkaline with sodium carbonate, and the ketone which separated distilled out with steam. The distillate was extracted with ether, this evaporated and the residue distilled in vacuum. At 15 mm. the boiling point was 68–70°, yield 9.6 g. of a colorless oil which proved to be nearly pure suberone. The semicarbazone prepared from it melted after one crystallization from methyl alcohol at 163–163.5°, sintering at 162'.

Anal. Subs., 2.455 mg.: 0.549 cc. of N (24°, 743 mm.), 0.0771 g.; CO_2, 0.1611; H_2O, 0.0641. Calcd. for $C_8H_{15}ON_3$: C, 56.76; H, 8.94; N, 24.85. Found: C, 56.99; H, 9.30; N, 25.13.

The mixed melting point with the semicarbazone of suberone (m. p. 163–163.5") which we prepared by dry distillation of barium suberate according to the directions of Day, Kon and Stevenson,[13] lay at 163–163.5°. The dibenzylidene compound melted at 107–108.5°.[12]

Anal. Subs., 0.1147: CO_2, 0.3670; H_2O, 0.0728. Calcd. for $C_{21}H_{20}O$: C, 87.45; H, 7.00. Found: C, 87.27; H, 7.10.

The mixed melting point with dibenzylidene suberone (from suberic acid) lay at 107–108.5°.

A second experiment, carried out with the same proportions of reagents and under the same conditions, gave the same products, but in slightly different ratio: 20 g. of cyclohexanone yielded in Fraction 1 (oxide), 1 g., Fractions 2 and 3 combined, 4.9 g., and from the bisulfite compound 11.9 g. of suberone.

Cyclopentanone and Diazomethane.—Twenty-three grams of cyclopentanone, purified through the semicarbazone (m. p. 212°), was treated with 22.5 g. of diazomethane under the conditions described in the cyclohexanone experiment. The product was worked up in an analogous way; from the bisulfite compound 14 g. of a ketone (suberone) of b. p. 69–70° (15 mm.) was obtained. The semicarbazone melted at 162–163°.

Anal. Subs., 0.1177: CO_2, 0.2458; H_2O, 0.0972; 2.792 mg. by 0.620 cc. of N (23°, 743 mm.). Calcd. for $C_8H_{15}ON_3$: C, 56.76; H, 8.94; N, 24.85. Found: C, 56.96; H, 9.24; N, 25.04.

The mixed melting point with suberone semicarbazone lay at 161–163°; the dibenzylidene compound melted at 107–108.5°, and showed no depression in melting point with that of suberone from suberic acid.

The portion of the reaction product which gave no bisulfite compound was distilled at 20 mm.; the oxide-containing fraction, boiling up to 45° (1 g.) was isomerized with zinc chloride as described. The distillate from this gave an intense color with fuchsin–sulfurous acid; with semicarbazide a mixture of semicarbazones was formed, probably those of cyclopentane aldehyde, hexahydrobenzaldehyde and cyclo-octanone. The separation of these was unsuccessful. The main portion of distillate, 6.5 g. of boiling point 45–110° (20 mm.), was in part treated with piperidine (see below), and in part converted to semicarbazone (cyclo-octanone), which melted at 165–166.5°.

Anal. Subs., 0.0834: H_2O, 0.0712; CO_2, 0.1805; 4.152 mg., 0.846 cc. of N (23°, 748 mm.). Calcd. for $C_9H_{17}ON_3$: C, 68.96; H, 9.36; N, 22.94. Found: C, 59.03; H, 9.55; N, 23.13.

It was not possible, even after repeated crystallization, to raise the melting point of this semicarbazone; that it consisted of nearly pure cyclo-octanone semicarbazone is shown both by the analysis and by the mixed melting point of 167.5–169° with the

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[13] Day, Kon and Stevenson, *J. Chem. Soc.*, 117,642 (1920).

semicarbazone prepared from our cyclo-octanone out of cyclohexanone and diazomethane as well as that obtained from Professor Ruzicka.

The reaction of the main portion of this fraction with piperidine did not yield homogeneous derivatives of the piperidino alcohol.

Summary

The action of diazomethane on cyclohexanone in the presence of methyl alcohol yields as the main product cycloheptanone, and in smaller quantities cyclo-octanone and an oxide isomeric with cycloheptanone.

Diazomethane with cyclopentanone leads (through cyclohexanone) to cycloheptanone as chief product, and cyclo-octanone as by-product. In this case, the oxide formed was not identified.

The reaction may be advantageously applied to the preparation of cycloheptanone and cyclo-octanone.

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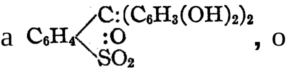
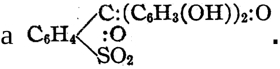
NOTES

Note on Catechol Sulfonephthalein.—Catechol sulfonephthalein, first mentioned by Moir,[1] was prepared by substantially the method of Lubs and Clark,[2] condensing at temperatures under 100 two moles of catechol with one mole of symmetrical dichloro derivative of o-sulfobenzoic acid, but omitting the use of zinc chloride as condensing agent. The resulting product was analyzed for sulfur, giving 95.71 and 95.76% of the calcd. for the formula  $C_6H_4\left\langle\begin{matrix}C:(C_6H_3(OH)_2)_2\\ :O\\ SO_2\end{matrix}\right.$, or 100.40 and 100.45% of the calcd. for the formula  $C_6H_4\left\langle\begin{matrix}C:(C_6H_3(OH))_2:O\\ :O\\ SO_2\end{matrix}\right.$. The product is amorphous, of a very deep purple color (practically black), solid but not brittle at ordinary temperatures, and moderately hygroscopic. When warmed to about 60° it is softened sufficiently to drop from a small stirring rod. Its solubilities are: miscible in all proportions with water; readily soluble in methanol, ethanol, acetone, glacial acetic acid and ethyl acetate; slightly soluble in ethyl acetoacetate, acetic aldehyde and ethyl ether; insoluble in benzene, toluene, xylene, petroleum ether, carbon disulfide, carbon tetrachloride, chloroform and acetic anhydride. Attempts at crystallization, using the first-named solvents, have been unsuccessful.

The aqueous solution of this product is found to give colors of but a fraction, about one-tenth, of the intensities of colors of other sulfonephthaleins. A noteworthy feature of several of these colors, and one not mentioned by Moir, is their tendency to change, in some cases in only a

[1] J. Moir, J. So. *Afr. Assoc. Anal. Chem.*, *3*, 6 (1920); C. *A.*, *14*, 3607 (1920).

[2] H. A. Lubs and W. M. Clark, J. *Wash. Acad. Sci.*, *5*, 609 (1915).

few minutes. In the following table are listed the colors exhibited by 0.2 cc. of a 0.5% aqueous solution of catechol sulfonephthalein when added to 10 cc. of the solutions listed in the first column.

	Immediate color	After 5 minutes	After SO minutes	After 1 hour	After 18 hours	After 36 hours
1.0 *N* HCl	Red	Red	Red	Red	Red	Red
0.01 N HCl	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
PH 5	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
*P*H 6	Yellow	Yellow	Yellow	Yellow	Yellow, slightly greenish	Yellowish-green
PH 7	Yellow, slightly greenish	Yellow, slightly greenish	Yellow, slightly greenish	Yellow, more greenish	Yellowish-green	Yellowish-green
PH 8	Purple, then indigo	Rich blue	Blue	Blue	Pale, inky	Yellowish-green
PH 9	Pinkish-purple	Pinkish-purple	Pinkish-purple	Pinkish-purple	Pinkish-purple	Yellowish-green
PH 10	Pinkish-purple	Pinkish-purple	Darker, surface cloudy	Less red, somewhat brownish	Light green	Yellowish-green
0.01 N NaOH	Indigo, becoming cloudy	Clear, fainter purple	Purple, surface green	Purple, surface green	Grass green	Pale green
1.0 *N*	Grass green	Grass green	Grass green	Grass green	Green, less intense	Pale green

The colors given by products of condensation of mixtures containing larger porportions (2.2 moles, 2.5 moles) of catechol are much the same as those shown in the table, save that the greens are much more intense.

It has been found possible to prepare a satisfactory series of color shades in the range *P*H 0 to *P*H 1.5.

Products condensed at temperatures of 130 and 160° were found to be incompletely soluble in water; these soluble portions give relatively very faint acid colors and comparatively more intense alkaline colors. Acidified aqueous solutions of the low temperature product, on vigorous boiling, showed similar color differences.

The product condensed at the lower temperature appears to be fairly pure, dilute and concentrated aqueous solutions remaining clear for many days, and no material is insoluble in sodium hydroxide[2] or in sodium bicarbonate[3] developing on long standing.

TAKOMA PARK
WASHINGTON, D. C.
CYRUS B. WOOD

RECEIVED FEBRUARY 21, 1930
PUBLISHED AUGUST 5, 1930

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[3] W. R. Orndorff and F. W. Sherwood, THIS JOURNAL, 45, 486 (1923).

A Note on the Preparation of **Monomethyldiethylmercaptoglucose.**—Monomethyldiethylmercaptoglucose can be obtained by treating the monosodium derivative of diethylmercaptoglucose with methyl iodide.

Emil Fischer[1] treated the monosodium diethylrnercaptoglucose with methyl iodide in the presence of methyl alcohol, and thought that he regained the original diethylmercaptoglucose. However, some oily disks were formed which he did not investigate. In the present work the sodium diethyimercaptoglucose was prepared according to Fischer's method by treating the diethylmercaptogiucose with sodium ethoxide. The excess of alcohol was evaporated and the methylation was done in absence of alcohol. The solid residue was refluxed with excess methyl iodide until ail dissolved. The excess of methyl iodide was evaporated and to the solid residue water was added. From this solution a substance was extracted by means of ether and chloroform which was recrystallized three times from absolute alcohol. It gave a melting point of 155°. The results of micro-analysis for carbon and hydrogen are given in the following table.

TABLE I

ANALYTICAL DATA FOR MONOMETHYLDIETHYLMERCAPTOGLUCOSE

Sample, mg	Weighed, mg.	Calcd. for, %	Found %
5 020	H_2O, 3 600	H, 8.05	8 03
	CO_2, 8.140	C, 43.97	44.21

The results seem to indicate that the monomethyldiethylmercaptoglucose as prepared by the above method is the same as that isolated by the present author,[2] as a by-product from the preparation of pentamethyldiethylmercaptoglucose.

CONTRIBUTION FROM THE
CHEMICAL, LABORATORY OF
WASHINGTON SQUARE COLLEGE
NEW YORK UNIVERSITY
NEW YORK, N. Y.

PHILIPPOS E. PAPADAKIS

RECEIVED MAY 23, 1930
PUBLISHED AUGUST 5, 1930

The Bromination of **Hexane.**—When the vapor of hexane is passed through bromine water, *p*-dibromobenzene and hexabromobenzene are said to be obtained.[1] F. O. Rice[2] has pointed out that such a transformation of hexane to an aromatic derivative seems doubtful. Since hexane spectroscopically free from benzene was available, it seemed desirable to investigate this question further.

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[1] E. Fischer, *Ber.*, 27,673 (1894).

[2] P. E. Papadakis, THIS JOURNAL,, 52,2147 (1930).

[1] Blair, Leabury and Wheeler, J. *Soc. Chem.* Ind., **43, 298T** (1924).

[2] F. O. Rice, "The Mechanism of Homogeneous Organic Reactions from the Physical-Chemical Standpoint," American Chemical Society Monograph, No. **39,** The Chemical Catalog Company, Inc., New York.

Pure (99.5%) nitrogen gas was first passed through concentrated sulfuric acid and bubbled through 20 g. of the pure hexane in a distilling flask. The arm of this flask was connected with a bubbler containing water with an excess of bromine. Five hours were required to vaporize the hexane, and examination of the bromine solution revealed no benzene bromides. Repeating with the bromine solution kept below zero and the hexane vaporized in the course of forty hours, no benzene bromides were found. A large amount of the hexane was recovered.

Repeating under the same conditions, but with the bromine solution exposed to a 100-watt Mazda lamp, again no benzene bromides were obtained.

When one gram of benzene was added to the hexane, and the vaporization carried out in the cold and in the dark, some benzene bromides were readily obtained.

The production of the derivatives mentioned in the literature can therefore be traced to hexane slightly contaminated with benzene.

This work was done at the suggestion of Dr. M. S. Kharasch, of the University of Chicago.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS.
FRANCIS M. PARKER

RECEIVED MAY 23, 1930
PUBLISHED AUGUST 5, 1930

Determination of Halogens in Organic Compounds.—We wish to thank Professor Robertson[1] for calling our attention to his papers, which we overlooked, probably because we were searching for a general method for the determination of chlorine, bromine and iodine and Robertson's method is, as he states, not suitable for iodine compounds.

We have tested his method using samples of about 0.15 g. of bromobenzene and obtained low results, a tendency to which Robertson also calls attention. Duplicates checked less closely than by our method.

The use of sodium peroxide instead of arsenite is obviously optional in either method, but the latter was decided upon after a trial of both reagents.

The time required depends upon whether the gravimetric or volumetric method is used. We needed eighty-five minutes by the gravimetric method with Robertson's apparatus.

The principal advantages of our method[2] are: (1) it is a general method applicable to compounds of chlorine, bromine and iodine.

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[1] Robertson, THIS JOURNAL, 52, **3023** (1930).

[2] Thompson and Oakdale, *ibid.*, 52, 1195 (1930).

(2) It can be used with low-boiling compounds such as ethyl bromide. (3) Metals in the residue may be very easily determined. (4) The accuracy is greater than in Robertson's method, as shown by a comparison of analyses. (5) The use of oxygen and platinized asbestos is never necessary. (6) There is no danger of the reaction becoming too violent or of the projection of particles onto the walls of the flask. (7) The time required is less, particularly because it has been found since publication of the last paper by Willard and Thompson,[3] that the apparatus described by them for the micro determination of halogens can also be used for samples as large as 0.1–0.2 g. This results in a saving of time as well as of space required for the apparatus. For samples of 0.01–0.02 g. an apparatus about half the size of this, or only 28 cm. high, works perfectly.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

J. J. THOMPSON
U. O. OAKDALE

RECEIVED JULY 17, 1930
PUBLISHED AUGUST 5, 1930

COMMUNICATIONS TO THE EDITOR

THE HEAT OF FORMATION OF MOLECULAR OXYGEN

Sir:

In a recent communication Copeland[1] has reported a value for the heat of formation of molecular oxygen of 165,000 cal. We have been engaged in a similar determination by an experimental method which differs only in minor details from the method used by Copeland. The results of our first determinations were in substantial agreement with those reported by Copeland, the average of a number of runs being about 160,000 cal. When we checked the method for possible errors we discovered that we were getting spurious heat effects in the calorimeter. When we took precautions to eliminate these heat effects we obtained as the average of a number of fairly consistent runs 131,000 cal. We do not find any evidence that metastable atoms reach the calorimeter.

CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

W. H. RODEBUSH
S. M. TROXEL

RECEIVED JUNE 27, 1930
PUBLISHED AUGUST 6, 1930

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[3] Willard and Thompson, THIS JOURNAL, 52, 1893 (1930).

[1] Copeland, ibid., 52, 2581 (1930).

THE HEAT OF DISSOCIATION OF OXYGEN

Sir:

Mecke[1] and Henri[2] have noted two regions of predissociation in the absorption spectrum of NO_2, the first becoming prominent around 3700 Å., corresponding to dissociation into NO and 0 , and the second beginning at 2447 Å. with NO and O' (excited O) as the products of dissociation. The value 3700 Å. (77,000 cal. per einstein) combined with the heat of reaction $NO_2 = NO + {}^1/_2O_2 - 13,000$ cal. yields them a heat of dissociation of oxygen of 128,000 cal. Kondvat'ev,[3] with the scheme

$$
\begin{aligned}
NO_2 &= NO + O' - 116,000 \\
O_2 &= O + O' - 162,000 \\
NO_2 &= NO + {}^1/_2O_2 - 13,000
\end{aligned}
$$

obtains 118,000 cal. as the heat of dissociation.

I find that excess CO_2 does not lower the quantum yield in the photochemical decomposition of NO_2 into NO and O_2 by λ4047 Å., which thus indicates a non-collisional mechanism for this reaction. This is further proved by photochemical experiments at low pressures; the quantum yield shows no falling off down to 0.01 mm. It must be concluded that absorption of λ4047 will lead to dissociation into NO and O. Therefore the heat of dissociation of oxygen appears to be as low as 115,000 cal., in satisfactory agreement with the value 118,000 cal. found by Kondvat'ev. The implication of a quantum yield lower than unity, actually found with 4047, in the interpretation of diffuse spectra will be examined in the extended report now in preparation.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

WARREN P. BAXTER[4]

RECEIVED JUNE 30, 1930
PUBLISHED AUGUST 5, 1930

CATALYSIS OF THE THERMAL DECOMPOSITION OF SILVER OXALATE BY SILVER SULFIDE

Sir:

It has been shown by one of us [S. E. Sheppard, "Colloid Symposium Monograph," 1925, Vol. III, p. 76] that minute traces of silver sulfide formed on the silver halide grain of photographic emulsions have a powerful sensitizing effect for the formation of the latent photographic image. This sensitizing action is manifested in two ways. The more important is a general sensitizing for all wave lengths to which the silver halide is itself sensitive, or for which it has been optically sensitized by dyes.

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[1] Mecke, *Naturwissenschaften*, 51,996 (1929); *Z. physik. Chem.*, *7B*, 108 (1930).

[2] Henri, *Nature*, 125,202 (1930).

[3] Kondvat'ev, *Z. physik. Chem.*, *7B*, 70 (1930).

[4] National Research Fellow in Chemistry.

Beside this, under certain circumstances, silver sulfide can act as an optical sensitizer for silver halide, like colloidal silver. The condition for the optical sensitizing appears to be a very high dispersity of the silver sulfide on and in the silver halide, and a relatively large amount of this highly dispersed silver sulfide. A number of hypotheses have been proposed to account for this sensitizing action, several of which have been discussed by one of the authors [*cf.* S. E. Sheppard, "Sixth Hurter and Driffield Memorial Lecture," *Phot. J.*, 68, 397 (1928); also Phot. *J.*, 70, 132 (1930)]. It has appeared to us that further light on the problem might be obtained by investigating the possible catalysis by silver sulfide of other reactions of silver salts. The thermal decomposition of silver oxalate

$$Ag_2C_2O_4 \longrightarrow 2Ag + 2CO_2$$

which has been studied by J. N. Macdonald and C. N. Hinshelwood [J. *Chem. Soc., 127, 2764* (1925)] was tried first. Normally this reaction proceeds solely at the interface with silver nuclei, and shows a typical autocatalytic course. It was reported recently by A. P. Benton and L. Cunningham [paper read at the Physical and Inorganic Chemistry Section, American Chemical Society, April, 1930] that illumination by ultraviolet light produces silver nuclei which effectively catalyze the reaction.

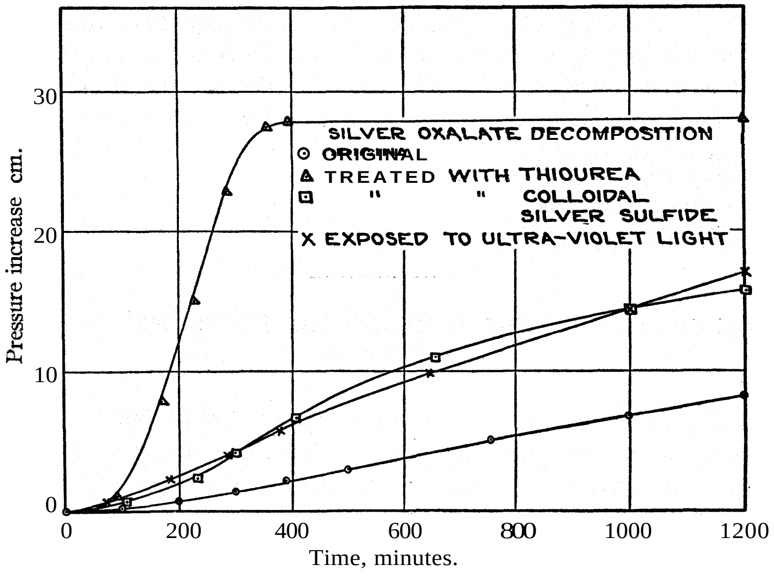

Fig. 1.

We have produced *silver sulfide nuclei* on silver oxalate by various methods and have found *silver sulfide* to be a very effective catalyst for the reaction, as shown by the graphs in Fig. 1.

A very marked diminution of the induction period is brought about. The extent of the catalysis evidently depends, in large degree, upon the dispersity of the silver sulfide. Although there is, in consequence of the decomposition, immediate accretion of silver to the silver sulfide nuclei, yet it appears evident that the latter are quite capable of replacing silver nuclei as catalytic phase.

According to the Ostwald–Langmuir conception of these heterogeneous reactions, the reaction should proceed only at the three-phase boundary line, gas:solid I:solid II. G. Adhikari and J. Felman [Z. *physik.* Chem., 131, 347 (1928)] have demonstrated actual "adlineation" in the case of the reaction

$$Hg + I_2 \longrightarrow \underset{\text{adsorption}}{Hg : I_2} \longrightarrow HgI_2$$

but they note that a physical theory which makes this result comprehensible is still lacking. The fact that silver sulfide can replace silver in the present reaction, as topochemically isomorphous, may give a clue to the mechanism, which will be discussed in a fuller report. Meanwhile, the replaceability of silver by silver sulfide in catalyzing the thermal decomposition of silver oxalate, where it can hardly act as an "acceptor" of carbon dioxide, makes less probable the "halogen acceptor" hypothesis proposed by K. C. D. Hickman [*Phot. J.*, 67, 34 (1927)] for its photosensitizing effect with silver halides. Also it makes more doubtful the special photoelectrolytic theory of A. P. H. Trivelli [J. Franklin *Inst.*, **204**, 649 (1927); **205**, 111 (1928)]. The bearing of the present results on photosensitizing will be discussed in a fuller publication.

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S. E. SHEPPARD
W. VANSELOW

RECEIVED JUNE 30, 1930
PUBLISHED AUGUST 5, 1930

ASSOCIATION POLYMERIZATION AND THE PROPERTIES OF ADIPIC ANHYDRIDE

Sir:

Faith in the existence of the once widely accepted hypothetical phenomenon, association polymerization, appears to have been revived (or strengthened) in the minds of some of its proponents by the discovery[1] of a spontaneously reversible relationship between a biosan (?) and a polysaccharide. No certain examples of this phenomenon have ever been adduced among materials of known structure, although its supposedly

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[1] Reilly and Donovan, *Sci. Proc. Roy. Dublin Soc.*, 19, 409 (1930); Schlubach and Elsner, Ber., 63, 362 (1930); Vogel, *ibid.*, 62, 2980 (1929); Pringsheim, Reilly and Donovan, *ibid.*, 62, 2379 (1929). It now appears, however, that these observations may be capable of quite a different interpretation. See Berner, *ibid.*, 63, 1356 (1930).

diagnostic features are clearly presented by certain six-membered cyclic esters.[2]

Adipic anhydride, recently studied by Dr. Julian W. Hill in this Laboratory, has already been described[3] as a solid melting at 97°, but the published evidence concerning its molecular weight is equivocal. It has now been found that adipic anhydride as prepared by the usual methods is polymeric. Its melting point varies considerably with accidental details of its preparation. It cannot be distilled as such, but on being heated in vacuo it is partially depolymerized, and the resulting (7-ring) monomer can be distilled. The latter is a colorless liquid that freezes at about 20°. It reverts spontaneously to the polymeric form. The reversion is catalyzed by traces of water: when it is poured into a not especially dried glass vessel, a scum of the polymer is formed at the walls within a few minutes.

The monomer and the polymer are sharply differentiated by their chemical behaviors. Both react practically instantaneously with aniline at room temperature; but the former yields only adipic acid monoanilide, whereas the latter yields a mixture of adipic acid, adipic acid monoanilide and adipic acid dianilide. The formation of dianilide (in 25% of the theoretical amount) constitutes a direct and decisive demonstration of the presence in the polymer of a series of adipyl residues united in a linear fashion by anhydride linkages

$$CO{-}(CH_2)_4{-}CO{-}O{-}CO{-}(CH_2)_4{-}CO{-}O{-}CO(CH_2)_4{-}CO{-}O{-}\text{etc.}$$

Thus the existence of a very high degree of mobility in the relationship between a monomer and its polymer does not preclude the intervention of real primary valence forces in the process or the presence of a definite macro-molecular chemical structure in the polymer, even though the monomer may not be unsaturated in the usual sense.

A more detailed report of the study of adipic anhydrides will be submitted at an early date.

EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON, DELAWARE

WALLACE H. CAROTHERS

RECEIVED JULY 2, 1930
PUBLISHED AUGUST 5, 1930

THE PHOTOCHEMICAL OXYGEN–CARBON MONOXIDE REACTION

Sir:

We have been studying the photochemical oxygen–carbon monoxide reaction and wish to announce some of our results. At room temperature in a mixture of oxygen and carbon monoxide and with light-producing

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[2] Carothers and Van Natta, THIS JOURNAL, 52, 318 (1929); Carothers, Dorough and Arvin, *ibid.*, 52, 3292 (1930).

[3] Voermann, *Rec. trav. chim.*, [2] 23, 265 (1904); Farmer and Kracovski, *J. Chem. Soc.*, 680 (1927).

oxygen atoms, the reaction goes almost quantitatively with the formation of ozone. A comparison with equivalent mixtures of oxygen and nitrogen shows that of the two possible reactions of initially formed oxygen atoms, $O + O_2 + X = O_3 + X$ and $O + CO + X = CO_2 + X$, the first goes at least 100 times faster. As both reactions are exothermic and probably do not require activation energy the above result should be attributed to the necessity for the oxygen atom and the carbon monoxide molecule to be properly oriented at the moment of collision, while the oxygen atom and the oxygen molecule can react more independently of their relative orientation in a similar triple collision.

Some years ago Coehn and Tramm [*Ber.*, 54, 1148 (1920)] reported that at room temperature water vapor has no influence on the rate of the photochemical oxygen–carbon monoxide reaction. We have repeated their experiments at 575° with the result that at this temperature water vapor has a very pronounced accelerating effect on the rate. This action is probably due to setting up of semi-thermal chains and may be linked with the well-known action of water in the thermal explosions of the carbon monoxide–oxygen mixtures. Further experiments on this subject are in progress and will be reported later in THIS JOURNAL.

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PRINCETON UNIVERSITY
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W. F. JACKSON
G. B. KISTIAKOWSKY

RECEIVED JULY 5, 1930
PUBLISHED AUGUST 5, 1930

THE OXIDATION OF LACTAL

Sir:

M. Bergmann[1] states that when lactal is oxidized with perbenzoic acid 4-galactosido-mannose is produced in good yield. His experimental results indicate that solely this sugar is formed in the reaction. For the pure sugar he finds the value $[\alpha]_D^{23} + 23.04$ in water five minutes after solution, the rotation becoming constant at +30.0 after about eighty minutes. In the autumn of 1929 we undertook the preparation of a considerable quantity of 4-galactosido-mannose for the purpose of studying the rotations of the sugar and some of its derivatives. The beautifully crystalline lactal which was prepared showed $[\alpha]_D^{20} + 27.69$ in water, in full agreement with Bergmann's measurement (+27.70). The substance did not reduce Fehling's solution and was therefore free of sugar. Its oxidation by a solution of perbenzoic acid in ethyl acetate, following Bergmann's directions, gave a good yield of a crystalline sugar the initial and final rotations of which corresponded well with his data, previously quoted. When the product, which absorbed no bromine and therefore contained no residual

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[1] M. Bergmann, Ann., 434, 79 (1923).

lactal, was fractionally recrystallized it proved to be a mixture of at least two sugars, one having a final $[\alpha]_D$ less than 30° and the other a greater value, Many repetitions of the work gave the same result. The mixture of sugars was dissolved in the minimum amount of water and allowed to crystallize slowly after the addition of methyl alcohol, thus separating the product: into two fractions. After five such fractionations the extreme values for the high and low fractions were $[\alpha]_D$ 34.6 and 26.9 (stable aqueous solutions). It is evident therefore that a review of Bergmann's data for 4-galactosido-mannose is required. We suppose that this sugar predominates in the lower-rotating fraction. What then is the identity of the higher-rotating sugar? It is apparently not lactose because it shows upward mutarotation and is very soluble in cold water. The separation of the sugars by fractional crystallization is tedious and considerable time will probably be required for the completion of the work. We are accordingly publishing this record of our year's studies on the subject. The experiments will be resumed in the fall of 1930, and it is also planned to make a similar study of the oxidation of cellobial and similar substances.

NATIONAL INSTITUTE OF HEALTH
WASHINGTON, D. C.

ANDREW J. WATTERS
C. S. HUDSON

RECEIVED JULY 9, 1930
PUBLISHED AUGUST 5, 1930

NEW BOOKS

The Analytical Expression of the Results of the Theory of Space Groups. By RALPH W. G. WYCKOFF. Second edition. Carnegie Institution of Washington, Washington, D. C., 1930. 239 pp. 222 figs. 17.5 X 25.5 cm.

The tabulation of the special positions of the space groups has been useful in facilitating the determinations of atomic arrangements in crystals. The second edition of this work has been modified to include a graphical presentation of the symmetry elements of the space groups together with statements of the symmetry properties of the special positions. C. Hermann's recently proposed nomenclature is included in the outline of the derivation of the space groups. The majority of the errors in the tables of the first edition have been corrected.

STERLING B. HENDRICKS

Trattato di **Chimica Organica.** (Treatise on Organic Chemistry.) By GIUSEPPE ODDO, Professor of Chemistry at the University of Palermo. Casa Editrice Remo Sandron, Palermo, Italy, 1930. xv + 949 pp. 101 figs. 17.5 X 25 cm. Price, L. 90.

It is doubtful whether or not an elementary textbook of organic chemistry can be expected to serve at the same time as a reference work for the advanced student. Most American textbook writers have contented themselves with a brief survey of the subject and have placed much emphasis on making it attractive to the beginner. These books are unsuitable for the advanced student. This is undoubtedly one reason for the great popularity of the more comprehensive textbooks which have been translated from German. Professor Oddo's treatise is of the latter type. It is one of the most complete treatments of the subject which has appeared in a single volume.

The book offers little that is novel either in the subject matter or the manner in which it is organized. The order of topics is the traditional one and the material is handled in a very conservative manner. The writer has concentrated his attention rather upon making the work terse, accurate and readable. In this he has succeeded admirably. Despite the vast amount of information included, the book is so attractively written that when one examines it for a particular bit of information he is likely to find himself continuing to read far beyond the point at which his immediate interest ceased.

It is to be regretted that the author has not seen fit to take advantage of certain recent developments in our ideas of valence. In the treatment of the "onium" compounds, at least, one might expect to find the electron theory used. Yet the nitrogen atom in ammonium compounds is still written as pentavalent.

But for this exception the work is thoroughly up to date. Especial care has been taken to mention recent industrial developments. The reviewer knows of no volume on the subject which is better adapted than this one to the needs of the advanced student.

REYNOLD C. FUSON

Outlines of Biochemistry. The Organic Chemistry and the Physico-Chemical Reactions of Biologically Important Compounds and Systems. BY ROSS AIKEN GORTNER, Professor of Agricultural Biochemistry in the University of Minnesota. John Wiley and Sons, Inc., New York, 1929. xv + 793 pp. 133 figs. 15.5 X 23.5 cm. Price, $6.00.

The author has performed an important service in the preparation of this book, It covers much material not found in other texts, with which biochemists need become better acquainted, namely, a very full and modern treatment of the colloidal state, to which is devoted 290 pages (slightly more than the whole of Kruyt's well-known text); and has valuable chapters dealing with the following groups of substances, of especial interest in the chemistry of plant tissues, the pectic substances contributed by J. J. Willaman, tannins, plant pigments and essential oils. Besides these distinctive chapters, the treatment of proteins, carbohydrates, fats and lipides, vitamins and enzymes, which together makes up the remainder of the work, seems to the reviewer sound, accurate and, in many respects, admirable. The form of presentation is attractive and stimulating.

The sub-title of the book, "The organic chemistry and the physico-chemical reactions of biologically important compounds" correctly indicates its content and viewpoint. The volume is based upon a course of lectures, developed during a period of seventeen years, for students in the department of Agricultural Biochemistry at the University of Minnesota. The illustrative material is drawn naturally rather more from agriculture and inanimate phenomena than from animal biochemistry. It will probably be for some time a standard book in connection with plant physiology, a subject badly in need of development. Also for use as the chemical preparation for a thorough course in general physiology, Gortner's book would be admirable. Such a combined course would doubtless be a better preparation for later specialization in some division of biochemistry than most graduate students now receive. On the other hand, it may be questioned whether still better preparation may not be had by the study of colloidal phenomena in a special course as a topic of physical chemistry, leaving room for some consideration of chemical physiology as a part of the course in biochemistry. Especially to all students devoting themselves to biochemistry who lack sound preparation in colloid science and to all teachers of the subject, Gortner's book is warmly recommended. The numerous references, each with full title, to journal articles, and the selected list of monographs, constitute a valuable bibliography. Work from the author's laboratory is perhaps given disproportionate notice, but this attests a first-hand knowledge by the author of the material presented.

Illustrations are abundant; the type, printing and binding are very good.

A few minor errors have been noted. On page 107 it is stated that PH is decreased on adding base to a solution. A number of statements on page 106 should be qualified. On page 226 "carbohydrates are partially burned, giving rise to lactic acid" is misleading; and the statement that rigor mortis is hastened by an atmosphere of oxygen is erroneous. The reviewer is not acquainted with evidence for the statement on the same page that a "contracted muscle invariably has a higher water content than does a relaxed muscle." The statement on page 429 that "any appreciable quantities of these β-ketonic acids are indicative of a serious pathological condition" is, unless qualified, erroneous. The structure given on page 453 for glutathione is now known to be incorrect.

This work is not suitable for use as a text with classes of medical students or others interested mainly in animal biochemistry, unless supplemented by much other material covering the broad field of correlation of chemistry to function and metabolism. To cite an illustration, although the section on carbohydrates, so far as it goes, is excellent, including an interesting treatment of photosynthesis, the metabolism of carbohydrate is largely neglected. Only ten lines are devoted to glycogen. Insulin is mentioned only once, to record the fact that glutose fails to relieve insulin convulsions. It is unfortunate that more material is not included from the field of animal metabolism and chemical correlation of function, not for its medical bearing but by reason of its purely scientific interest and importance as a part of biochemistry.

In his preface Professor Gortner expresses the following opinion: "In most of the Universities of America the development of the field of biochemistry has been left very largely to the group interested in the medical aspects. Accordingly, in a very large measure the biochemistry of the American Universities is not biochemistry in its strictest sense, but rather leans more and more toward the field of human pathology. Most medical school biochemistry could be more correctly designated as human pathological chemistry." Recognizing the need of departments of physiological chemistry in association with medical schools, he says, "It should likewise be recognized that there is a necessity for a study of the fundamental reactions underlying the broader field of biology, the primary object of which is to study and investigate the chemical and physicochemical reactions which take place in the normal biological organism, whether that organism be animal or plant." With the last quotation most biochemists will heartily agree, though many will also maintain that the point of view advocated has long been the attitude of a large number of American students even of "human pathological chemistry." The universality of knowledge and the interdependence of nearly all departments of biology upon nearly all divisions of physical science is perhaps more widely appreciated by biochemists in medical schools than Professor Gortner realizes. His book will nevertheless aid in spreading that important doctrine. The reviewer would suggest that phytochemistry also may profit from closer contact with both physiological and pathological chemistry.

PHILIP A. SHAFFER